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THERMAL EXPANSION OF CRYSTALS

Part V. Hæmatite

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Received September 4, 1950

(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. INTRODUCTION

FOR crystals with trigonal structure, such as hæmatite, the linear thermal expansion coefficient is not independent of the direction in the lattice as in the case of isotropic crystals. The expansion of the lattice can, however, be calculated from a knowledge of two independent coefficients $\alpha_{\parallel}$ and $\alpha_{\perp}$, which refer respectively to the directions parallel and perpendicular to the principal trigonal axis; the corresponding expansion coefficient, α_{θ}, is in accordance with the relation stated by Voigt (1910),

$$\alpha_{\theta} = \alpha_{\parallel} \cos^2\theta + \alpha_{\perp} \sin^2\theta.$$

Forrestier (1928) studied the volume dilatation of ferric oxide, a synthetic product prepared in the laboratory, but such determination is of little significance as it does not elucidate the very interesting question of the anisotropic expansion in various directions in the crystal. Moreover, the anisotropy of thermal expansion indicates an intimate relationship to the chemical forces and the orientation of the molecules. Such information is of considerable value in analysing the nature of mechanism of the changes during expansion and since a knowledge of the anisotropic expansion is of great importance in the theory of the solid state, the author has undertaken a series of measurements of the expansion of this crystal in several directions of known orientation in the crystal.

2. EXPERIMENTAL TECHNIQUE

Of the several methods which have been employed for the measurement of the linear expansion of small non-cubic specimens, that which is capable of the greatest accuracy is Fizeau's interferometric method. This method, despite its obvious advantages, has been little used for expansion measurements on anisotropic non-metallic crystals. This is partly due to the necessity for continuous observation of the fringe movement extending over long periods of time, but principally because of the difficulty of the construction of three spacers for each orientation which, in practice, means that they should be cut, as far as possible, from one single specimen.

In the present investigation the author has employed the modified form of the interferometric method as previously employed by him for the determination of the expansion coefficients of isotropic crystals (Sharma, 1950).

3. Preparation of Spacers

Groth (1905) gives the ratio of the axes of hæmatite, $a : c = 1 : 1 \cdot 3654$, and the interfacial angle α, where the principal axis passes through the vertex as 85°42′. Thus with the help of a contact goniometer it was extremely easy to locate this vertex. The specimens at the disposal of the author were of two categories—one of a reddish brown colour and the other of blackish brown variety and of a more compact composition. Before cutting the sections a preliminary determination of the specific gravity of the latter type was undertaken, and crystals having the same specific gravity were chosen. A small slab was cut from a large crystal so that the normal to the surface coincided with the direction along which the expansion was to be measured. Three small pyramids of exactly the same height were prepared from the slab. Although this method of preparation does not orient the specimens with great accuracy it proved to be quite satisfactory for the present investigation. No differential expansion of spacers, indicating changes in their orientation, could be detected from the configuration of the interference pattern which remained unaltered throughout the whole heating process.

4. Results

The expansion was measured in three different directions; perpendicular to the principal trigonal axis, parallel to it, and perpendicular to the rhombo-

Table I

Coefficient of linear expansion for hæmatite parallel to the trigonal axis

$\alpha_{\parallel} = 0 \cdot 0_5 7897 + 0 \cdot 0_8 5285\, t + 0 \cdot 0_{11} 7318\, t^2$

Temperature (° C.)	$\alpha_{\parallel} \cdot 10^6$ (Observed)	$\alpha_{\parallel} \cdot 10^6$ (Calculated)	Difference (%)
53·2	8·28	8·20	+1·0
89·6	8·43	8·43	..
124·7	8·65	8·67	−0·2
158·4	8·96	8·92	+0·5
190·6	9·26	9·17	+1·0
221·8	9·44	9·43	..
252·2	9·66	9·69	−0·3
281·8	9·89	9·97	−0·8
310·5	10·24	10·24	..
338·2	10·52	10·52	..
368·3	10·88	10·83	+0·5
400·6	11·27	11·19	+0·7

TABLE II

Coefficient of linear expansion for hæmatite perpendicular to the trigonal axis

$$\alpha_{\perp} = 0{\cdot}0_5 7834 + 0{\cdot}0_7 1047\, t + 0{\cdot}0_{10} 1172\, t^2$$

Temperature (°C)	$\alpha_{\perp} \cdot 10^6$ (Observed)	$\alpha_{\perp} \cdot 10^6$ (Calculated)	Difference (%)
46·7	8·34	8·34	..
78·9	8·72	8·73	..
109·1	9·23	9·12	+1·2
137·7	9·43	9·50	−0·7
165·3	9·78	9·89	−1·1
194·8	10·25	10·32	−0·7
225·9	10·80	10·80	..
255·3	11·36	11·27	+0·8
283·3	11·82	11·74	+0·7
312·8	12·27	12·26	..
343·6	12·89	12·82	+0·6
373·0	13·41	13·37	+0·3
403·7	13·80	13·97	−1·2

TABLE III

Coefficient of linear expansion for hæmatite perpendicular to the rhombohedral faces

$$\alpha_{\theta} = 0{\cdot}0_5 7843 + 0{\cdot}0_8 8952\, t + 0{\cdot}0_{10} 1016\, t^2$$

Temperature (°C)	$\alpha_{\theta} \cdot 10^6$ (Observed)	$\alpha_{\theta} \cdot 10^6$ (Calculated)	Difference (%)
44·6	8·24	8·26	−0·2
76·2	8·63	8·58	−0·6
106·0	8·98	8·91	+0·8
134·5	9·25	9·23	+0·2
161·8	9·56	9·56	..
191·4	9·82	9·93	−1·1
222·8	10·40	10·34	+0·6
252·5	10·86	10·75	+1·1
281·1	11·14	11·16	..
311·5	11·53	11·62	−0·8
343·3	11·93	12·11	−1·5
378·6	12·69	12·69	..

hedral faces $(10\bar{1}1)$ and $\bar{(}10\bar{1}1)$. According to Dana (1911), $(0001 \wedge 10\bar{1}1 = 57°34'4'')$, hence this is also the angle between the trigonal axis and the normal to the rhombohedral face along which the expansion has been measured.

Tables I–III give the values of the coefficients of linear expansion in the various directions. Values calculated from the interpolation formulæ are

also inserted for comparison. The variation of α's with temperature is depicted graphically in Fig. 1.

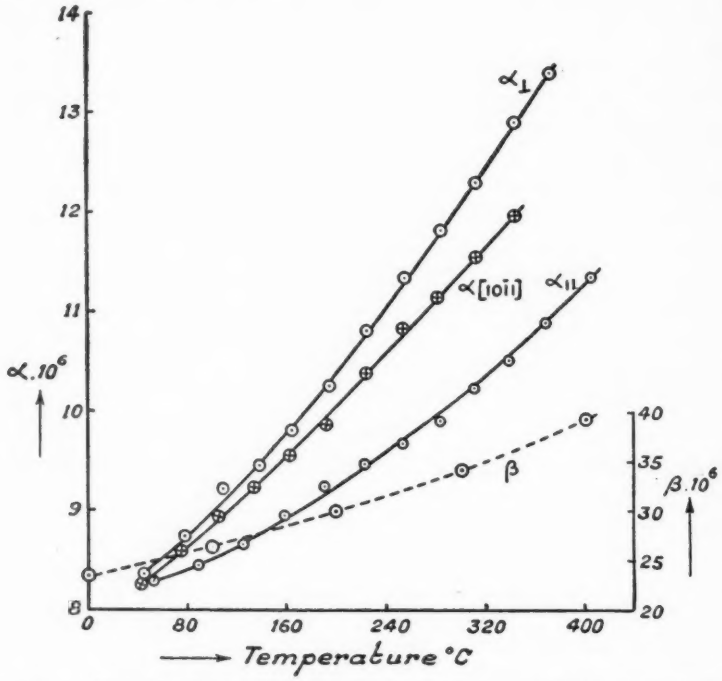

FIG. 1. Variation of the coefficients of expansion for hæmatite with temperature

5. DISCUSSION

The most striking result of the above investigation is the very low anisotropy of thermal expansion of hæmatite at the room temperature. Thus at 25 °C., $\alpha_{\parallel} = 8{\cdot}03 \times 10^{-6}$ and $\alpha_{\perp} = 8{\cdot}10 \times 10^{-6}$. The crystal structure of hæmatite has been fully described by Bragg (1937) and the lattice belongs to the isosthenic type in which atoms or ions are linked to all their neighbours with bonds of the same strength. The elastic deformability of such a lattice parallel to the principal Z-axis will be nearly equal to that perpendicular to it. This may be written in terms of the elastic modulii $S_{11} \approx S_{33}$. The elastic constants of hæmatite have been determined only by Voigt (1910) (quoted by Hearmon, 1946) according to whom $S_{11} = 4{\cdot}41 \times 10^{-13}$ cm.²/dyne and $S_{33} = 4{\cdot}43 \times 10^{-13}$ cm.²/dyne (both at 20° C).

However, the rate of variation of the coefficient of linear expansion parallel to the trigonal axis is much smaller than that perpendicular to it, so that the anisotropy increases with elevation of temperature; thus at 400° C. $\alpha_{\parallel} = 11 \cdot 18 \times 10^{-6}$ while $\alpha_{\perp} = 13 \cdot 90 \times 10^{-6}$. The trends of the curves in Fig. 1 also bring out this fact clearly.

An inspection of the interpolation formulæ for these two directions reveals a very interesting feature. Although the middle and the last coefficients in the formula for $\alpha_{\perp}$ are higher than those for $\alpha_{\parallel}$, the magnitude of the first coefficient is reversed. In consequence of this, at 0° C. the coefficient of expansion perpendicular to the axis is less than that parallel to it. Thus in between this temperature and the room temperature there must be a temperature at which these coefficients attain equality. A simple calculation shows that at about 12° C. the two expansions become exactly equal ($7 \cdot 96 \times 10^{-6}$). Thus at this temperature the thermal anisotropy vanishes and the crystal behaves like an isotropic substance.

The data for the successive runs gave results which showed that the effects observed were unquestionably reproducible. It can further be shown that the data for the three directions are consistent within themselves. According to the cosine-square law the expansion coefficient in a crystal having trigonal symmetry is a linear function of the square of the cosine of the angle between the direction of measurement and the principal trigonal axis. The expansion coefficients at a number of temperatures for the three directions studied are plotted against $\cos^2\theta$ in Fig. 2. In plotting the curves no correction has been made for the change in the angle θ with temeperature, but for the set of measurements in the direction perpendicular to the rhombohedral faces it has been assumed to be 57°34′ the value at room temperature, throughout. The neglect of this change is justified by the fact that it is quite small and introduces an uncertainty less than that in the orientations of the specimens along and perpendicular to the axis. It is obvious from the figure, however, that the results are consistent among themselves within the limit of experimental error. It may be added that at 12° C. the coefficient of expansion perpendicular to the rhombohedral faces comes out to be $7 \cdot 95 \times 10^{-6}$ which is remarkably close to the value obtained for $\alpha_{\parallel}$ and $\alpha_{\perp}$ at the same temperature.

It is also possible to evaluate the volume coefficient of expansion, β, from the expressions along the direction of the crystallographic axes. Thus β is equal to $\alpha_{\parallel} + 2\alpha_{\perp}$. The values of β so calculated at different temperatures are entered in Table IV and the variation with temperature is depicted graphically by the dotted curve in Fig. 1.

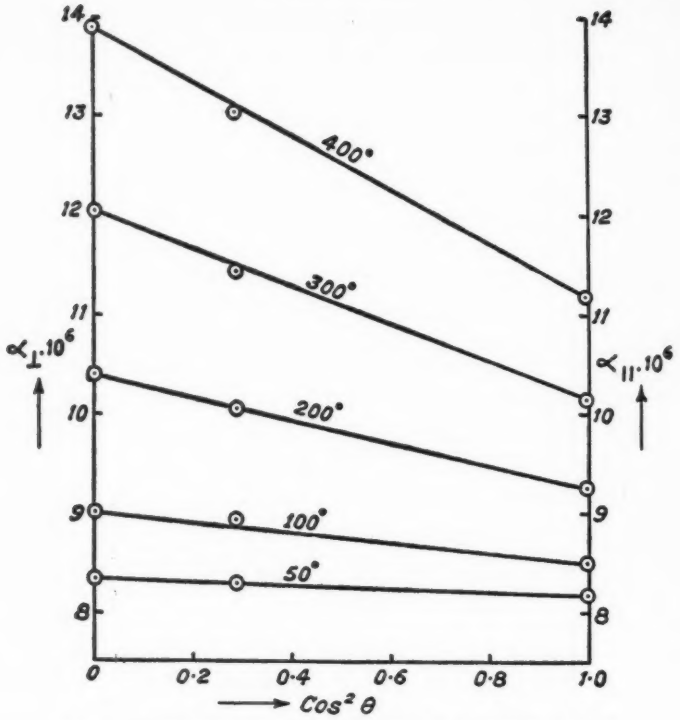

FIG. 2. True expansion coefficient plotted as a function of $\cos^2\theta$

TABLE IV

Variation of β for hæmatite with temperature

$\beta = 0{\cdot}0_4 2355 + 0{\cdot}0_7 2650\, t + 0{\cdot}0_{10} 3016\, t^2$

Temperature ..	0° C.	100° C.	200° C.	300° C.	400° C.
$\beta \cdot 10^6$ ..	23·55	25·50	30·05	34·20	38·98

Unfortunately no comparison of these values of β can be made, as Forrestier's paper, referred to above, does not provide any numerical data, nor can the curves reproduced therein be put to any interpolation.

In conclusion the author thanks Professor R. S. Krishnan for his guidance and keen interest in the work.

The author's thanks are also due to Dr. C. S. Pichamuthu, Director of the Geological Survey of Mysore, for kindly loaning the crystals.

6. Summary

With the help of interferometric method the thermal expansion of hæmatite has been studied perpendicular and parallel to the trigonal axis and perpendicular to the rhombohedral faces. The principal coefficients of expansion are given by

$$\alpha_{\parallel} = 0{\cdot}0_5 7897 + 0{\cdot}0_8 5285\, t + 0{\cdot}0_{11} 7318\, t^2$$

$$\alpha_{\perp} = 0{\cdot}0_5 7834 + 0{\cdot}0_7 1047\, t + 0{\cdot}0_{10} 1172\, t^2$$

The results show that $\alpha_{\parallel}$ is slightly greater than $\alpha_{\perp}$ at 0° C.; it is exactly equal at 12° C., and slightly less at the room temperature; and that both $\alpha_{\parallel}$ and $\alpha_{\perp}$ steadily increase with temperature over the whole range of temperature (upto 400° C.). Further, Voigt's cosine-square-law is verified.

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Groth	..	*Chem. Krystallographie*, 1906, **1**, 105.
Hearmon	..	*Rev. Mod. Phy.*, 1946, **18**, 409.
Sharma	..	*Proc. Ind. Acad. Sci.*, **A**, 1950, **31**, 83.
Voigt	..	*Lehrbuch der Krystallphysik*, 1910.

AZOIC DYES

Part X. Brominated Naphthols

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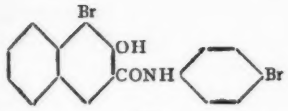
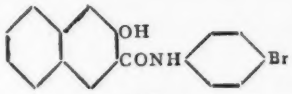
Received July 6, 1950

Among the "naphthols" commercially available for azoic dyeing is a bromo derivative: Brenthol BA (I.C.I.), the 4-bromo-*o*-anisidide of 2-hydroxy-3-naphthoic acid. Brenthol BA has medium substantivity to cellulose and gives red combinations of good fastness to light and chlorine. The present work is concerned with the bromination of certain anilides of hydroxy-naphthoic acid, the object being to determine the orientation of the bromine atoms and the effect of bromination on the shades and fastness properties of the azoic dyeings produced from the brominated "naphthols". The "naphthols" employed for bromination were Brenthol AS, AS-FR and AS-PA, which are the anilide, *o*-anisidide and *p*-anisidide respectively of 2-hydroxy-3-naphthoic acid.

Brenthol AS was brominated with bromine (2 mols.) in acetic acid;[1] the product was a dibromo compound, which underwent partial debromination and gave a monobromo compound on heating in acetic acid solution with granulated tin and hydrochloric acid.[2] Applied as a "naphthol" and developed with Fast Scarlet GG, Red B and Blue BB salts (the three diazonium salts which have been used for developing all the "naphthols" in the present work) it gave bright scarlet, bordeaux and reddish blue shades with light fastness 7, 6, 6, chlorine fastness 4, 4, 4-5, soda boil fastness 3, 3-4, 5, and rubbing fastness 3-4 respectively. In order to determine whether the bromine atom is in the naphthalene or benzene nucleus, the monobromo compound was hydrolysed with boiling 16-17% alcoholic caustic potash for 15 hours. The acid was identified as 2-hydroxy-3-naphthoic acid, and the amine as *p*-bromaniline. Thus, by direct bromination of Brenthol AS the first bromine atom enters the naphthalene nucleus in the 1-position, since it is known that this can be easily removed by reducing agents[1,2] and the second bromine atom enters the benzene nucleus. The dibromo compound and its partially debrominated derivative can therefore be assigned the structures (I) and (II) respectively.

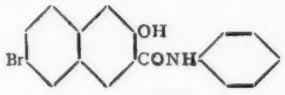


(I)



(II)

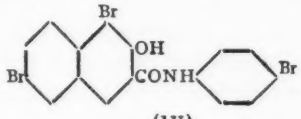
6-Bromo-2-hydroxy-3-naphthanilide (III) was prepared by condensing 6-bromo-2-hydroxy-3-naphthoic acid with aniline in presence of phosphorus trichloride. 6-Bromo-2-hydroxy-3-naphthoic acid was prepared by brominating 2-hydroxy-3-naphthoic acid to obtain 1 : 6-dibromo-2-hydroxy-3-naphthoic acid and subsequently heating it with tin and hydrochloric acid to effect partial debromination. A method described in a patent[3] for partial debromination is to heat the monoalkali salts of 1 : 6-dibromo-2-hydroxy-3-naphthoic acid to 100° with alkali sulphites. As a "naphthol",



(III)

(III) gave with the usual three diazonium salts bright scarlet, bordeaux and reddish blue shades possessing light fastness 6-7, 5-6, 6, chlorine fastness 4-5, 4, 4-5, soda boil fastness 3-4, 3, 5 and rubbing fastness 4, 3-4, 3-4 respectively. The shades from (II) and (III) were brighter than the corresponding shades from Brenthol AS.

Brenthol AS was then treated with three mols. of bromine to obtain a tribromo compound, which on partial debromination gave a dibromo compound whose properties were studied in comparison with those of the monobromo compounds, 6-bromo- and 4′-bromo-2-hydroxy-3-naphthanilide; the position occupied by the second bromine atom was also determined. The dibromo compound gave with the usual three diazonium salts bright scarlet, bordeaux and reddish blue shades with light fastness 6-7, 5-6, 5-6, chlorine fastness 5, 4-5, 5, soda boil fastness 3-4, 3-4, 5, and rubbing fastness 3-4, 4, 3-4 respectively. Hydrolysis with alcoholic caustic potash solution gave 6-bromo-2-hydroxy-3-naphthoic acid and *p*-bromaniline. The tribromo and dibromo compounds are therefore constituted as 1 : 6 : 4′-tribromo- and 6 : 4′-dibromo-2-hydroxy-3-naphthanilide (IV and V).



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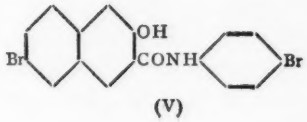
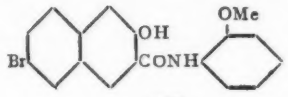


(V)

These brominated "naphthols" appear to have technical interest in view of the brightness and fastness of the azoic shades. While this work was in progress, *FIAT Final Report 1313, Vol. III,* became available. It is stated in this Report that, among a very large number of new 'naphthols' with different substituents in the aryl nuclei which were prepared, the only one of interest was the *o*-anisidide (VI) of 6-bromo-2-hydroxy-3-naphthoic acid. The 'naphthol' (VI) gave brighter shades in some cases than those obtained with standard



(VI)

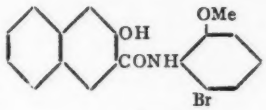
"naphthols", and the light fastness was higher by ½ to 1 point on the standard 1-8 scale. The blues obtained in conjunction with Fast Blue BB and Fast Blue RR and the violet with Fast Violet B were of special interest. In general the new brominated Naphtol gave azoic shades which were "unusually fast to bleach and light".

The bromination of Brenthol FR (Naphtol AS-OL) was next studied. The dibromo compound obtained with two mols. of bromine was partially debrominated by the usual method to yield a monobromo compound, which gave with the usual three diazonium salts bright scarlet, bordeaux and reddish blue shades with light fastness 6-7, 6, 6, chlorine fastness, 5, 4-5, 5, soda boil fastness 3-4, 3-4, 5 and rubbing fastness 3-4 respectively. The acid obtained on hydrolysis of the monobromo compound was 2-hydroxy-3-naphthoic acid and the semi-solid amine, which contained bromine, gave after three crystallizations from dilute alcohol, a small quantity of a solid (A) m.p. 86-88°. Its mixed m.p. with 4-bromo-*o*-anisidine (98°; obtained by the hydrolysis of Brenthol BA) was intermediate between the melting points of the amine (A) and 4-bromo-*o*-anisidine. The mixed m.p. of monobromo-2-hydroxy-3-naphth-*o*-anisidide with Brenthol BA was similarly between the melting points of the two.

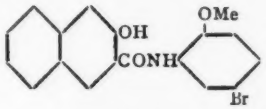
The next approach was to brominate Brenthol FR with 3 mols. of bromine and subsequently debrominate the tribromo compound to obtain dibromo-2-hydroxy-3-naphth-*o*-anisidide, the amine from which might provide a clue regarding the course of bromination with 2 mols. of bromine. The amine obtained by the hydrolysis of this dibromo-2-hydroxy-3-naphth-*o*-anisidide was identified by m.p. and analysis to be 3:4-dibromo-*o*-anisidine. A small amount of 6-bromo-2-hydroxy-3-naphthoic acid was isolated from the acid residue of the "naphthol", indicating that tribromination of Brentho FR gave a mixture of products. The dibromo-2-hydroxy-3-naphth-*o*-anisi-

dide gave with the usual three diazonium salts bright scarlet, bluish red and dark blue shades which bled appreciably on soaping and possessed light fastness 6-7, 5-6, 6, chlorine fastness 5, soda boil fastness 5, 4, 5 and rubbing fastness 4, 3-4, 3-4 respectively.

From the isolation of 3:4-dibromo-*o*-anisidine from the hydrolytic products of dibromo-Brenthol FR, it appears probable that during the dibromination of Brenthol FR the first bromine atom enters the 1-position in the naphthalene ring and the second bromine atom attacks partly the 3- and partly the 4-position in *o*-anisidine. Thus, the product obtained after debromination is a mixture of (VII) and Brenthol BA. This would explain



(VII)



Brenthol BA

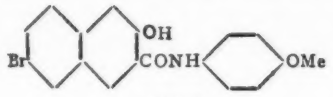
the mixed m.p.s of the amine (A) with 4-bromo-*o*-anisidine and the mixed m.p. of monobromo-2-hydroxy-3-naphth-*o*-anisidide with Brenthol BA.

Attempts were then made to separate this mixture. The monobromo-Brenthol FR was coupled with diazotized aniline, but it has not been possible so far to effect the separation of the two dyes in this mixture by fractional crystallization or by chromatography. The amine (A) was then converted into the 2:4-dinitrodiphenylamine derivative by treatment with 2:4-dinitrochlorobenzene. By fractional crystallization of this derivative from alcohol, 2-methoxy-5-bromo-2′:4′-dinitrodiphenylamine (the dinitrophenyl derivative of 4-bromo-*o*-anisidine) was isolated and identified, but not the isomer from 3-bromo-*o*-anisidine. The mother liquor on dilution gave a mixture.

6-Bromo-2-hydroxy-3-naphth-*o*-anisidide (VI), the azoic shades from which possess excellent fastness properties,[4] was prepared by condensing 6-bromo-2-hydroxy-3-naphthoic acid with *o*-anisidine. The product gave scarlet, bordeaux and reddish blue shades with the usual three diazonium salts, having light fastness 6, 6, 5-6, chlorine fastness 4-5, 4, 5, soda boil fastness 3, 3-4, 5, and rubbing fastness 3-4 respectively.

The behaviour of Brenthol PA (2-hydroxy-3-naphth-*p*-anisidide) was then studied. The dibromo derivative, on partial debromination by the usual method, yielded a monobromo compound which gave with the usual three diazonium salts scarlet, bordeaux and reddish blue shades with light fastness 7, 6, 6, chlorine fastness 5, soda boil fastness 3-4, 3-4, 5, and rubbing fastness 4 respectively. Both the acid and the amine obtained on hydrolysing

this monobromo compound were found to contain bromine, indicating that during dibromination a mixture of two products is formed. On the basis of Bargellini's observation[5] that when both the hydroxyl and the amino groups are blocked by an alkyl and acyl group respectively (*e.g.*, as in acet-*p*-anisidide), the first halogen atom enters *ortho* to the alkoxyl group, the structures (VIII) and (IX) can be assigned to the mixture of products obtained by dibromination of Brenthol PA and subsequent debromination. The product (VIII) (6-bromo-2-hydroxy-3-naphth-*p*-anisidide), synthesized from the



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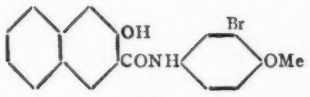
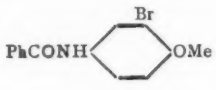


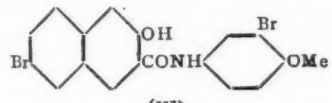
(IX)

corresponding acid and *p*-anisidine, gave with the usual three diazonium salts scarlet, bordeaux and bright blue shades with light fastness 6, 5-6, 5-6, chlorine fastness 5, 4-5, 5, soda boil fastness 4, 3-4, 5 and rubbing fastness 3-4 respectively.

The dibromo-2-hydroxy-3-naphth-*p*-anisidide obtained by the partial debromination of the tribromo compound gave with the usual three diazonium salts scarlet, bordeaux and dark blue shades possessing light fastness 6, 5-6, 5-6 chlorine fastness 5, 4-5, 5, soda boil fastness 3-4, 3-4, 5, and rubbing fastness 4 respectively. The amine obtained on the hydrolysis of the dibromo compound was converted into the benzoyl derivative, m.p. 149°, which was



(X)



(XI)

identified as N-benzoyl-2-bromo-*p*-anisidine (X). The acid proved to be 6-bromo-2-hydroxy-3-naphthoic acid (m.p. 263-64°). The dibromo-2-hydroxy-3-naphth-*p*-anisidide, obtained by partial debromination of the tribromo compound, was therefore constituted as (XI).

All the brominated "naphthols" synthesized in the present work are characterized by high fastness to light, chlorine, soda boil and rubbing. 6-Bromo-2-hydroxy-3-naphth-*o*-anisidide[4] does not possess any special advantage over the "naphthols" obtained by the bromination and partial debromination of Brenthol AS, FR, PA. A closer comparison of (III), (VI) and (VIII), which are the anilide, *o*-anisidide and *p*-anisidide respectively of 6-bromo-2-hydroxy-3-naphthoic acid, shows that it is rather difficult to decide which of these is superior in the fastness of the azoic shades, since all

of them have an average light fastness of the grade 6-7, chlorine fastness 4-5, rubbing fastness 3-4 for all the dyeings, soda boil fastness 3-4 for the scarlet and red dyeings and 5 for the blue dyeings. The "naphthols" (III) and (VI) however give dyeings which are more attractive than those from (VIII) which contains a *p*-methoxyl group.

A similar comparison of the three "naphthols", 6-bromo-, 4′-bromo- and 6:4′-dibromo-2-hydroxy-3-naphthanilide, with regard to the general appearance of the shades produced by them and their fastness properties, reveals that the dibromo-2-hydroxy-3-naphthanilide has no advantage over the monobromo compounds (II) and (III). This is also true of the monobromo and dibromo compounds obtained from Brenthol FR and PA by bromination and subsequent partial debromination.

Experimental

1:4′-Dibromo-2-hydroxy-3-naphthanilide (I)

To a suspension of Brenthol AS (2·63 g., 1 mol.) in glacial acetic acid (20 c.c.), bromine (1·2 c.c., 2 mols. and 10% excess) in acetic acid (5 c.c.) was added slowly at room temperature during 30-45 minutes. The flask was vigorously shaken during the addition. The mixture was then heated under reflux till the evolution of hydrobromic acid ceased (about 2½ hours). The solution after cooling was poured into water (300 c.c.), the product filtered, washed and dried. The substance (4 g.) crystallized from glacial acetic acid in yellowish brown plates, m.p. 233-34° (Found: Br, 38·4. $C_{17}H_{11}O_2NBr_2$ requires Br, 38·0%).

4′-Bromo-2-hydroxy-3-naphthanilide (II)

A mixture of the dibromo compound (I; 2·8 g.), acetic acid (25 c.c.)-granulated tin (1·58 g.), commercial hydrochloric acid (3·2 c.c.) and 10% copper sulphate solution (10 c.c.) was heated under reflux for 14 hours. The product was then poured into water (300 c.c.), filtered and the residue washed free from acid. It was dissolved in alcoholic caustic soda (10%), filtered, and the filtrate acidified with dilute hydrochloric acid. The precipitate was filtered, washed free from acid and dried (2·1 g.). The substance crystallized from acetic acid in colourless plates, m.p. 250-51° (Found: Br, 23·8. $C_{17}H_{12}O_2NBr$ requires Br, 23·4%).

Hydrolysis of (II) with alcoholic caustic potash

A solution of the product (II) (1·4 g.) in 16% alcoholic caustic potash (10 c.c.) was heated under reflux for 15 hours, cooled, diluted with an equal volume of water, and acidified with dilute hydrochloric acid. The precipi-

tate (A) was filtered off and the acidic filtrate was concentrated and made alkaline with caustic soda. Benzoyl chloride (1·5 c.c.) was added and the mixture was vigorously shaken, keeping it distinctly alkaline. The precipitate was filtered, washed free from alkali and crystallized from alcohol (norit). The colourless shining flakes had m.p. 203-04°, and was identified as benz-*p*-bromoanilide.

The precipitate (A) was treated with 15 c.c. of 10% sodium bicarbonate solution and filtered. The filtrate was acidified and the precipitate collected and crystallized from dilute alcohol. The yellow shining plates melted at 215-16°, did not contain bromine, and the mixed m.p. with 2-hydroxy-3-naphthoic acid was not depressed.

1 : 6-*Dibromo*-2-*hydroxy*-3-*naphthoic acid*

A solution of 2-hydroxy-3-naphthoic acid (11·2 g.) and bromine (7·2 c.c.) in glacial acetic acid (100 c.c.) was refluxed for 3 hours. The solution was cooled and poured into water (600 c.c.). The yellow product was filtered, washed free from acid and dried (20·5 g., m.p. 245-47°). It crystallized from acetic acid in yellow needles, m.p. 249-249·5° (m.p. 246°).[6]

6-*Bromo*-2-*hydroxy*-3-*naphthoic acid*

A mixture of the 1 : 6-dibromo acid (20 g.), acetic acid (125 c.c.), granulated tin (14·7 g.), conc. hydrochloric acid (29·4 c.c.) and 10% copper sulphate solution (5 c.c.) was refluxed for 12-13 hours. On pouring into water the product was collected (15·5 g.) and crystallized from acetic acid. The glistening plates had m.p. 263-64° (m.p. 262° in ref. 5).

-*Bromo*-2-*hydroxy*-3-*naphthanilide* (*III*)

The acid (13·3 g., 1 mol.) was suspended in dry toluene (100 c.c.) containing aniline (5·5 c.c.) and the mixture heated to 60-70°. Phosphorous trichloride (5 c.c.) in toluene (10 c.c.) was addad during half an hour, and the reaction mixture maintained at this temperature for 1 hour. It was then heated under reflux for 12-13 hours when the evolution of hydrochloric acid gas ceased. Sodium carbonate (4 g. as 10% solution) was then added, the toluene steam-distilled, and the residue filtered. After purification by dissolving in alcoholic caustic soda, filtering and reprecipitating with hydrochloric acid, the substance (13·0 g.) crystallized from dilute acetic acid in plates, m.p. 277-78° (Found: N, 4·2. $C_{17}H_{12}O_2NBr$ requires N, 4·1%).

1 : 6 : 4′-*Tribromo*-2-*hydroxy*-3-*naphthanilide* (*IV*)

Brenthol AS (5·26 g., 1 mol.) was brominatad in acetic acid (80 c.c.) with bromine (3·78 c.c., 3 mols. and 15% excess). The product (9·9 g.),

which was worked up in the usual manner, crystallized from acetic acid in yellow plates, m.p. 217-18° (Found: Br, 48·4. $C_{17}H_{10}O_2NBr_3$ requires, Br, 48·0%).

6: 4'-*Dibromo-2-hydroxy-3-naphthanilide* (*V*)

The tribromo compound (IV; 5·8 g.) was heated in acetic acid (50 c.c.) with granulated tin (2·9 g.), conc. hydrochloric acid (5·8 c.c.) and 10% copper sulphate solution (1 c.c.) for 16-17 hours. The product (4·85 g.) crystallized from nitrobenzene in needles, m.p. 295-96° (Found: N, 3·0; Br, 37·6. $C_{17}H_{11}O_2NBr_2$ requires N, 3·3; Br, 38·0%).

Hydrolysis of (*V*)

The "naphthol" (2·5 g.) was treated with caustic potash (4·8 g.) in alcohol (50 c.c.) at the boil for 24 hours. The acid and the amine were isolated in the usual manner. The acid (0·6 g.), which contained bromine, crystallized from dilute alcohol in shining plates, m.p. 263-64°, undepressed by admixture with 6-bromo-2-hydroxy-3-naphthoic acid. The amine contained bromine, and the benzoyl derivative crystallized from dilute alcohol in colourless lustrous flakes, m.p. 203-04°, which was also the m.p. after admixture with benz-*p*-bromoanilide.

Dibromo-2-hydroxy-3-naphth-o-anisidide

Brenthol FR (5·86 g., 1 mol.) was brominated in acetic acid (40 c.c.) with bromine (2·3 c.c. in 10 c.c. acetic acid). The product (8·4 g.) was crystallized twice from acetic acid (norit), and the pale yellow needles had m.p. 162-63° (Found: N, 3·3; Br, 35·0. $C_{18}H_{13}O_3NBr_2$ requires N, 3·1; Br, 35·5%).

Monobromo-2-hydroxy-3-naphth-o-anisidide

The above product (5·8 g.) was debrominated in acetic acid (40 c.c.) with tin (4·75 g.), commercial hydrochloric acid (9·5 c.c.) and 10% copper sulphate solution (2·5 c.c.). The product (3·6 g.) crystallized from glacial acetic acid in rods, m.p. 194-95° (Found: N, 3·4; Br, 21·7. $C_{18}H_{14}O_3NBr$ requires N, 3·8; Br, 21·5%).

Hydrolysis of monobromo-2-hydroxy-3-naphth-o-anisidide

The "naphthol" (4 g.) was treated with boiling 12·8% alcoholic caustic potash for 30 hours. The acid and the amine were isolated in the usual manner. The acid, which did not contain bromine, crystallized from dilute alcohol in yellow shining plates; m.p. and mixed m.p. with 2-hydroxy-3-naphthoic acid was 219-21°. The semi-solid amine (0·9 g.) was treated with sodium acetate

(2 g.), and 2:4-dinitrochlorobenzene (0·9 g.) in boiling alcohol (15 c.c.) for 2-3 hours. After dilution with an equal volume of water, the red product was filtered, washed with alcohol, dried, and extracted with hot alcohol (30 c.c.). The alcohol-insoluble portion (0·3 g., m.p. 230-35°) crystallized from glacial acetic acid in red, shining plates, m.p. 240-41°, not depressed by admixture with the dinitrophenyl derivative of 4-bromo-*o*-anisidine prepared by the same method. The alcoholic mother liquor on dilution with water gave a product (m.p. 150-66°) which was a mixture.

Tribromo-2-hydroxy-3-naphth-o-anisidide

Brenthol FR (8·79 g.) was brominated in glacial acetic acid (75 c.c.) with bromine (5·2 c.c.; 3 mols. and 5% excess in 25 c.c. acetic acid). The product (15·5 g.) crystallized from glacial acetic acid (norit) in dull brownish yellow plates, m.p. 213-14° (Found: Br, 45·7. $C_{18}H_{12}O_3NBr_3$ requires Br, 45·3%).

Partial debromination of tribromo-2-hydroxy-3-naphth-o-anisidide

The tribromo compound (12 g.) was heated in acetic acid (75 c.c.) with tin (9·6 g.), conc. hydrochloric acid (19·2 c.c.) and 10% copper sulphate solution (5 c.c.) for 12-13 hours. The product (9·0 g.) crystallized from acetic acid in light yellow rectangular plates, m.p. 232-34° (Found: Br, 35·1. $C_{18}H_{13}O_3NBr_2$ requires Br, 35·5%).

Hydrolysis of dibromo-2-hydroxy-3-naphth-o-anisidide

The dibromo compound (5 g.) was boiled with 16% alcoholic caustic potash (50 c.c.) for 27 hours. The amine and the acid were isolated in the usual manner. The amine (1·1 g.) crystallized from dilute alcohol (norit) in colourless plates, m.p. 103-04° (Found: Br, 56·7. $C_7H_7ONBr_2$ requires Br, 56·9%). The benzoyl derivative crystallized from dilute alcohol (norit) in needles, m.p. 140–41° (Found: N, 4·0. $C_{14}H_{11}O_2NBr_2$ requires N, 3·6%). The amine was identified as 3:4-dibromo-*o*-anisidine, for which the m.p. recorded in the literature is 103°; the m.p. cited for the benzoyl derivative is 137-38°.

The acid crystallized from alcohol in shining plates, m.p. 262-63° and was identified by its m.p. and mixed m.p. to be 6-bromo-2-hydroxy-3-naphthoic acid. The alcoholic mother liquor on dilution with water gave a product which also contained bromine and melted at 200-02°, unchanged by further crystallizations from dilute alcohol. It was found to be a mixture of 2-hydroxy-3-naphthoic acid and its 6-bromo derivative.

6-Bromo-2-hydroxy-3-naphth-o-anisidide (VI)

Prepared from 6-bromo-2-hydroxy-3-naphthoic acid (2·67 g.), *o*-anisidine (2·5 c.c.) and phosphorous trichloride (1 c.c.) in toluene by the usual method, the product (2·5 g.) crystallized from glacial acetic acid in greenish yellow needles, m.p. 186-187° (Found: N, 4·1. $C_{18}H_{14}O_3NBr$ requires N, 3·8%).

Dibromo-2-hydroxy-3-naphth-p-anisidide

Brenthol PA (8·79 g.) was brominated in acetic acid (60 c.c.) with bromine (3·3 c.c., 2 mols.). The product (11·9 g.) crystallized from glacial acetic acid in plates, m.p. 176-78° (Found: N, 2·9; Br, 35·2. $C_{18}H_{13}O_3NBr_2$ requires N, 3·1; Br, 35·5%).

Partial debromination of dibromo-2-hydroxy-3-naphth-p-anisidide

The dibromo compound (9·45 g.) was debrominated by heating in acetic acid (50 c.c.) with granulated tin (7·7 g.), conc. hydrochloric acid (15·4 c.c.) and 10% copper sulphate solution (4 c.c.) for 12-13 hours. The purified product (8 g.) crystallized from dilute acetic acid (norit) in plates, m.p. 212-14° (Found: N, 3·9; Br, 21·0. $C_{18}H_{14}O_3NBr$ requires N, 3·8; Br, 21·5%).

Hydrolysis of monobromo-2-hydroxy-3-naphth-p-anisidide

The monobromo compound (3·5 g.) was boiled with 16% alcoholic caustic potash for 24 hours. The amine and the acid were isolated in the usual way. The acid, which contained bromine, crystallized from alcohol (norit) in shining plates, m.p. 261-63°, undepressed by admixture with 6-bromo-2-hydroxy-3-naphthoic acid. The alcoholic mother liquor on dilution with water gave a product (m.p. 207-10°) which contained bromine. This was a mixture of 2-hydroxy-3-naphthoic acid and its 6-bromo derivative. The amine, converted into its benzoyl derivative (0·85 g.), crystallized from dilute alcohol (norit) in plates, m.p. 125-27°, unchanged by further crystallizations from the same solvent. It contained bromine and the mixed m.p. with benz-*p*-anisidide (m.p. 152-53°) was 137-40° indicating that it was a mixture of benz-*p*-anisidide and its bromo derivative.

6-Bromo-2-hydroxy-3-naphth-p-anisidide (VIII)

Prepared from 6-bromo-2-hydroxy-3-naphthoic acid (1·34 g.), *p*-anisidine (0·74 g.) and the phosphorous trichloride (1 c.c.) in toluene (35 c.c.) by the usual method, the product (0·85 g.) crystallized from nitrobenzene in light brownish grey plates, m.p. 296-97° (Found: N, 4·3. $C_{18}H_{14}O_3NBr$ requires N, 3·8%).

Tribromo-2-hydroxy-3-naphth-p-*anisidide*

This was prepared from Brenthol PA (8·79 g.) and bromine (5·2 c.c., 3 mols.) in acetic acid. The product (15·4 g.) crystallized from glacial acetic acid (norit) in greenish yellow plates, m.p. 234–35° (Found: Br, 45·0. $C_{18}H_{12}O_3NBr_3$ requires Br, 45·3%.)

Partial debromination of tribromo-2-hydroxy-3-naphth-p-*anisidide*

The tribromo compound (12 g.) was heated in acetic acid (100 c.c.) with granulated tin (9·6 g.), conc. hydrochloric acid (19·2 c.c.) and 10% copper sulphate solution (5 c.c.) for 12-13 hours. The product (10 g.) crystallized from acetic acid in colourless needles, m.p. 237-37·5° (Found: Br, 35·9. $C_{18}H_{13}O_3NBr_2$ requires Br, 35·5%).

Hydrolysis of dibromo-2-hydroxy-3-naphth-p-*anisidide*

The "naphthol" (5 g.) was boiled with 16% alcoholic caustic potash for 27 hours. The acid crystallized from dilute alcohol in shining plates, m.p. 263-64°, undepressed by admixture with 6-bromo-2-hydroxy-3-naphthoic acid. The amine was converted into the benzoyl derivative, which crystallized from dilute alcohol (norit) in needles, m.p. 148-49°, (Found: Br, 26·6. $C_{14}H_{12}O_2NBr$ requires Br, 26·2%). The substance was identified by mixed m.p. as N-benzoyl-2-bromo-*p*-anisidine (X).

N-acetyl-2-bromo-p-*anisidine*

Acet-*p*-anisidide (1 g., m.p. 129-31°), prepared by the acetylation of *p*-anisidine, was treated in chloroform (10 c.c.) with bromine (0·33 c.c., 1 mol.). Chloroform was removed by distillation and the sticky residue (0·8 g.) crystallized from water (norit) in plates, m.p. 110-11°.

N-benzoyl-2-bromo-p-*anisidine* (*X*)

The acetyl compound (0·5 g.) was boiled with 15 c.c. of dilute hydrochloric acid (1 : 1) for 2 hours. The solution was cooled, made alkaline and treated with benzoyl chloride (1·5 c.c.). The benzoyl derivative (0·65 g.) crystallized from dilute alcohol in needles, m.p. 149-50°, undepressed by admixture with the benzoyl derivative of the amine obtained by the hydrolysis of (XI).

Dye-trials and fastness properties

Dye-trials were carried out as described earlier[7] using the spirit-dissolving process for dissolving the "naphthols". The light fastness of the dyeings was examined by the method of the Society of Dyers and Colourists.[8] Determinations of the fastness to soda boil and chlorine were made according to the I.C.I. methods, while the rubbing fastness was examined by the Ciba method.[9]

Summary

The bromination of the anilide, *o*-anisidide and *p*-anisidide of 2-hydroxy-3-naphthoic acid has been studied. The orientation of the bromine atoms has been determined and the effect of bromination on the shades and the fastness properties of the azoic shades produced from the brominated "naphthols" has been examined. By bromination of the anilide, the first bromine atom enters the naphthalene nucleus in the 1-position, and this can be readily removed by reducing agents. The second bromine atom enters the benzene nucleus in the 4′-position, while the third bromine atom attacks the naphthalene nucleus in the 6-postion. Bromination of the *o*-anisidide gives a mixture of products; the first bromine atom enters the naphthalene nucleus, while the second bromine atom attacks partly the 3- and partly the 4-position in *o*-anisidine. Tribromination also gives a mixture in which 1:3′:4′-tribromo-2-hydroxy-3-naphth-*o*-anisidide predominates.

The monobromo derivative of the *p*-anisidide of hydroxynaphthoic acid, obtained by the partial debromination of its dibromo derivative, is a mixture of 6-bromo- and 2′-bromo-2-hydroxy-3-naphth-*p*-anisidide. The dibromo compound, obtained by the partial debromination of the tribromo derivative, is 6:2′-dibromo-2-hydroxy-3-naphth-*p*-anisidide.

The N-6-bromo-2-hydroxy-3-naphthoyl derivatives of aniline, *o*- and *p*-anisidine have been prepared by condensing 6-bromo-2-hydroxy-3-naphthoic acid with the amines.

All the brominated "naphthols" synthesized in the present work are characterized by the brightness and excellent fastness properties of the azoic shades.

Acknowledgment

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THE VIBRATION SPECTRUM OF RUTILE

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Introduction

Amongst the crystals of non-cubic symmetry, rutile has a particularly simple structure. It belongs to the holohedral form of the tetragonal class, of which large synthetic crystals are now available for study. A large clear crystal from the collection of Sir C. V. Raman has recently been used by Narayanan (1950) for the study of its Raman spectrum. The infra-red reflexion maxima from natural crystals were measured by Liebish and Rubens (1911). In the present paper the author has worked out its vibration spectrum from group theoretical considerations and has obtained the numerical values of the frequencies from approximate force constants.

2. Symmetry Modes of Rutile

Rutile belongs to the space group D_{4h}^{14}. The unit cell contains two titanium atoms in the positions 000, and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and four oxygen atoms in the positions $\pm(uuo)$ and $\pm(\frac{1}{2}-u, \frac{1}{2}-u, \frac{1}{2})$ where $u = \cdot 31$. The structure can be visualised very easily by considering two interpenetrating primitive tetragonal lattices of titanium atoms, the atoms of one occupying the body centres of the other. The atoms of oxygen are now placed at distances of $\cdot 31a\sqrt{2}$ on either side of titanium atoms along one of the face diagonals of the X – Y planes. This is done in such a way that the oxygen atoms in one of the titanium interpenetrating lattices are along one face diagonal, and in the second along the other face diagonal. If the atoms are projected on an X – Y plane the oxygen atoms of the one set will be on parallel lines parallel to one of the face diagonals and in the other set parallel to the other face diagonal. This is clearly seen in the Fig. 1 where the atoms have been projected in above manner.

The number of vibration frequencies and their symmetry types can be easily written down from the Character Table of the point group D_{4h} by the usual methods. Leaving aside the translations there are eleven frequencies, four of which are doubly degenerate. Four of these (A_{1g}, B_{1g}, B_{2g} and E_g) are active in the Raman Effect and six in the infra-red. One, namely A_{2g}

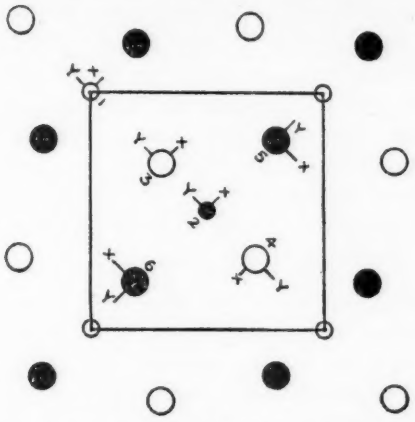

FIG. 1. Unit Cell of Rutile showing neighbours of atoms.
Large circles show the oxygens and small circles the titaniums. Shaded circles are atoms at level c/2 above the basal plane.

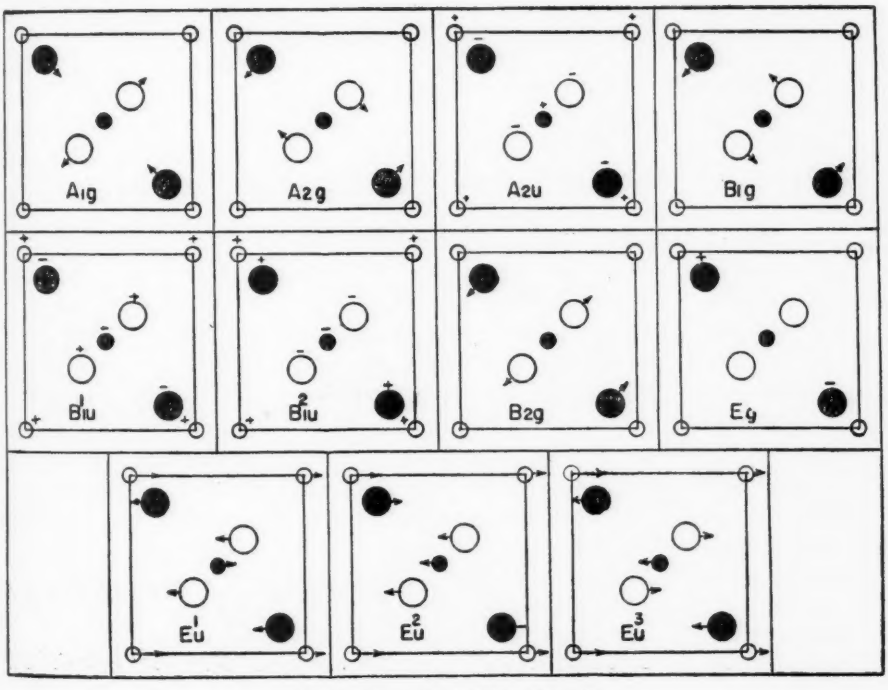

FIG. 2. Symmetry Modes of Rutile
Large circles show the oxygen atoms and the smaller circles the Titanium atoms, shaded circles are the atoms at a level c/2 above the basal plane.

is inactive in both. The six active frequencies in the infra-red fall into three symmetry types A_{2u}, B_{1u} and E_u. Of these, B_{1u} consists of two frequencies obtainable from a determinant of the second order, and E_u contains three doubly degenerate frequencies which are obtained on the solution of a third order determinant. All these symmetry modes have been represented in Fig. 2, where translations have been left out, and only one form of each degenerate frequency has been drawn. It will be seen that titanium atoms, being centres of symmetry, are all at rest in the Raman active modes, and in motion in the infra-red active ones.

The symmetry co-ordinates are given below. For the purpose of their description, Y axis of each atom (except of the titanium atom at the centre) has been taken along the face diagonal on which it lies, the positive direction of each being away from the centre of the cell. The X axis can be obtained by rotating the Y axis through a right angle in the clockwise direction. For the titanium atom at the centre of the cell, the axes are parallel to those of the titanium atom at the corner. The axes have been shown in the Fig. 1. M is the mass of a titanium and m that of an oxygen atom. Degenerate frequencies are distinguished by the letters (a) and (b).

Symmetry co-ordinates:—

A_{1g}: $y_3 + y_4 - y_5 - y_6$

A_{2g}: $x_3 + x_4 - x_5 - x_6$

A_{2u}: $z_1 + z_2 - \frac{M}{2m}(z_3 + z_4 + z_5 + z_6)$

B_{1g}: $x_3 + x_4 + x_5 + x_6$

$B_{1u}{}^1$: $z_1 - z_2 + z_3 + z_4 - z_5 - z_6$

$B_{1u}{}^2$: $z_1 - z_2 - \frac{M}{2m}(z_3 + z_4 - z_5 - z_6)$

B_{2g}: $y_3 + y_4 + y_5 + y_6$

$E_g{}^{(a)}$: $z_3 - z_4$

$E_g{}^b$: $z_5 - z_6$

$E^{1(a)}{}_u$: $(x_1 + y_1 + x_2 + y_2) - \frac{M}{2m}(x_3 + y_3 - x_4 - y_4 - x_5 + y_5 + x_6 - y_6)$

$E^{1(b)}{}_u$: $(x_1 - y_1 + x_2 - y_2) + \frac{M}{2m}(-x_3 + y_3 + x_4 - y_4 - x_5 - y_5 + x_6 + y_6)$

$$E^{2(a)}{}_u: \quad (x_1+y_1-x_2-y_2)+\frac{M}{2m}(x_3+y_3-x_4-y_4+x_5-y_5+y_6-x_6)$$

$$E^{2(b)}{}_u: \quad (x_1-y_1-x_2+y_2)+\frac{M}{2m}(-x_3+y_3+x_4-y_4+x_5+y_5-x_6-y_6)$$

$$E^{3(a)}{}_u: \quad (x_1+y_1-x_2-y_2)+(-x_3-y_3+x_4+y_4+y_5-x_5-y_6+x_6)$$

$$E^{3(b)}{}_u: \quad (x_1-y_1-x_2+y_2)+(x_3-y_3-x_4+y_4-x_5-y_5+x_6+y_6)$$

3. Evaluation of Frequencies

An exact evaluation of the frequencies requires a knowledge of the forces between an atom and as large number of other atoms as possible. Even in the simplest cases of cubic symmetry this requires a large number of force constants (Ramanathan, 1947). In the present case the number of constants involved becomes still larger on account of low symmetry. We will, therefore, use approximate methods, and only consider the forces existing between an oxygen and its twelve neighbours, and also those between a titanium atom and its fourteen neighbours.

The immediate neighbours of any oxygen or titanium atom can be easily identified from the Fig. 1, where the atoms have been projected on the basal plane—atoms at levels $\pm c/2$ being represented by the shaded circles. In this way each shaded circle represents two neighbours one above and the other below the X–Y plane. Each oxygen atom (*e.g.*, atom No. 3) is seen to be surrounded by three almost equidistant titaniums. One—for the atom 3, it is the atom No. 1—is at a distance of $\cdot 438a$ from it, while the other two which are at levels $\pm c/2$ are at distances $\cdot 422a$, where a is the length of the X or Y axes of the unit cell and c that of the Z axis. It follows that every titanium is surrounded by six oxygens, two at distances of $\cdot 438a$ are in the same X–Y plane and the four at $\cdot 422a$ are at levels $\pm c/2$. If the ratio of the axes, c/a were a few per cent. greater, all the six oxygen neighbours of a titanium would have been exactly equidistant from it, and we would have had one of the simplest and purely geometrical structure. It is, therefore, reasonable to assume that there is an attractive force, parallel to the Z axis, between a titanium and the four nearest oxygens (at distances of $\cdot 422a$), which has made the c axis slightly smaller than expected from purely geometrical considerations. For this reason, we divide the force arising out of the displacement of any of the six oxygen neighbours of a titanium into two parts. The first is due to the change in the titanium-oxygen distance and is assumed to involve the same force constant for all the six neighbours. The other part is due to the Z component of the dis-

placement of the four oxygens atoms. The change in the potential energy is thus given by

$$2V = \sum_{i=1}^{4} K_1 \Delta r_i^2 + \sum_{j=1}^{4} K_4 \Delta z_j^2,$$

where Δr_i is the change of the interatomic distance and Δz_j, the component of the displacement parallel to the fourfold axis. The second term can also be interpreted as that arising from the change of the angle formed by two oxygens with a titanium neighbour of a different plane. We, however, prefer the above form.

In addition to the above, each oxygen atom is surrounded by one oxygen atom, in the same XY plane, at a distance of $\cdot 532a$ and eight other oxygens at distances $\cdot 608a$. The change in the potential energy due to the displacement of these with respect to the first can be written as

$$2V = K_2 \Delta r^2 + \sum_{i=1}^{8} K_3 \Delta r_i^2$$

The first of these two terms plays such a minor part in the frequency expressions that we will put $K_2 = K_3$ without the possibility of any serious error. We are thus left with three force constants, which are the only ones necessary for the derivation of the Raman frequencies.

For the evaluation of the infra-red frequency we require the additional force constants due to the mutual displacements of the titanium atoms. The nearest titanium neighbours of a titanium atom are only two at levels $\pm c$, and are equivalent atoms always in phase with it. The next nearest titaniums are eight in number and occupy the centres of the cells $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$. The change in the potential energy due to the displacement of any of these is given by

$$2V = \sum_{1}^{8} K_5 \Delta r_i^2.$$

From these five force constants, which are reduced to four by putting $K_2 = K_3$ we get the following frequency expressions. m represents the mass of an oxygen atom and M that of a titanium.

Raman Active Frequencies:—

1. A_{1g} : $4\pi^2\nu^2 m = 1 \cdot 8\, K_1 + 2K_2 + \cdot 32K_3$
2. B_{2g} : $4\pi^2\nu^2 m = 1 \cdot 8\, K_1 + 2K_2 + 5 \cdot 3K_3$
3. B_{1g} : $4\pi^2\nu^2 m = \cdot 32K_3$
4. E_g : $4\pi^2\nu^2 m = \cdot 6K_1 + 2 \cdot 34K_3 + 2K_4$

Infra-Red Frequencies:—

5. A_{2u} : $4\pi^2\nu^2 = (4{\cdot}72\,K_1 + 8K_4)\left(\frac{M+2m}{4m\sqrt{M}}\right)^2$

6 and 7. B_{1u}: These are the roots of

$$\begin{vmatrix} c_{11} - \lambda\,(2M + 2m) & c_{12} \\ c_{21} & c_{22} - \lambda\left(\frac{M^2 + 2Mm}{m}\right) \end{vmatrix} = 0$$

where $c_{11} = 19K_1 + 32K_4 + 18{\cdot}3K_3 + 32K_5$

$$c_{22} = 4{\cdot}74\left(1 - \frac{M}{2m}\right)^2 K_1 + 8K_4\left(1 - \frac{M}{2m}\right)^2 + 19\frac{M}{2m}K_3 + 32\,K_5$$

$$c_{12} = c_{21} = 9{\cdot}5\left(1 - \frac{M}{2m}\right)K_1 + 8K_4\left(1 - \frac{M}{2m}\right) - 18{\cdot}3\,K_3 + 32\,K_5$$

8, 9, 10 E_u : These are the roots of the determinant

$$\begin{vmatrix} c_{11} - \left(\frac{M^2}{m} + 2M\right)\lambda & c_{12} & c_{13} \\ c_{21} & c_{22} - \left(\frac{M^2}{m} + 2M\right)\lambda & c_{23} \\ c_{31} & c_{32} & c_{33} - (4m + 2M)\lambda \end{vmatrix} = 0$$

where

$$c_{11} = 3{\cdot}62\,K_1\left(\frac{M}{2m} + 1\right)^2$$

$$c_{12} = C_{21} = 2\,K_1\left(\frac{M}{2m} + 1\right)^2 + 1{\cdot}62\,K_1\left[\left(\frac{M}{2m}\right)^2 - 1\right]$$

$$c_{13} = c_{31} = -\,3{\cdot}24K_1\left(\frac{M}{2m} + 1\right)$$

$$c_{22} = 2K_1\left(\frac{M}{2m} + 1\right)^2 + 1{\cdot}62\,K_1\left[\frac{M}{2m} - 1\right]^2 + 2{\cdot}56\,K_3\left(\frac{M}{2m}\right)^2 + 13{\cdot}1\;K_5$$

$$c_{23} = -\,3{\cdot}24\left(\frac{M}{2m} - 1\right)K_1 - 2{\cdot}56\,K_3\frac{M}{2m} + 13{\cdot}1\,K_5$$

$$c_{33} = 6{\cdot}48\,K_1 + 2{\cdot}56\,K_3 + 13{\cdot}1\,K_5$$

11. *Inactive Frequency*

A_{2g} : $4\pi^2\nu^2 m = 5{\cdot}3K_3$

4. Numerical Values of the Frequencies

The frequency expressions show that B_{2g} is the largest Raman frequency and that $A_{1g} > E_g \cdot B_{1g}$ is seen to be a very low frequency. The three prominently observed Raman frequencies (Narayanan, *l.c.*) are 565 cm.$^{-1}$, 441 cm.$^{-1}$ and 236 cm.$^{-1}$ which can be easily identified with B_{2g}, A_{1g} and E_g respectively. The three force constants can then be derived from them. The values used in this paper are given below. K_5 is only required in the infra-red frequencies and has been selected to give an accurate value of the observed compressibility.

$$K_1 = \cdot 65 \times 10^5 \text{ dynes/cm.}$$

$$K_2 = K_3 = \cdot 3 \times 10^5 \text{ dynes/cm.}$$

$$K_4 = -\cdot 24 \times 10^5 \text{ dynes/cm.}$$

$$K_5 = \cdot 31 \times 10^5 \text{ dynes/cm.}$$

The Raman frequencies calculated from these are given in Table I and the infra-red frequencies in Table II.

Table I. *Raman frequencies of rutile*

Symmetry type	Calculated ν cm.$^{-1}$	Observed ν cm.$^{-1}$
A_{1g} ..	441	440·8
B_{2g} ..	590	565
B_{1g} ..	249	236
E_g ..	101	..

Table II. *Infra-red frequencies of rutile*

Symmetry type	Direction of vibration	Calculated ν	Position of reflection maxima	Maxima observed with type of ray
A_{2u} ..	Parallel to tetragonal axis	39μ	..	..
B_{1u} ..	,,	29μ	30μ	Extraordinary ray
,, ..	,,	22μ	22μ (19μ, 16μ)	,,
E_u ..	Perpendicular to axis	106μ	..	..
, ..	,,	30μ	39μ	Ordinary ray
,, ..	,,	25μ	19μ (16μ, 15μ)	,,

Liebish and Rubens (*l.c.*) observed four infra-red reflection maxima in the extraordinary and four in the ordinary ray. In the table the former have been shown against those vibrations which are parallel to the tetragonal axis and the latter against those whose direction is perpendicular to it. The agreement between the observed and the calculated frequencies is fair, and confirms our assignment of the Raman frequencies. Further corroboration is possible by a study of the polarisation characteristics of the Raman spectrum.

5. Compressibility of Rutile

Let us suppose that the crystal is compressed so that all the interatomic distances decrease by $\frac{1}{n}$ of their length. The volume strain is $\frac{3}{n}$ and the change in potential energy per unit volume $\frac{1}{2}\left(\frac{3}{n}\right)^2 \frac{1}{k}$. where k is the compressibility. This has to be put equal to the change in the potential energy in a unit volume brought about by the alterations in the interatomic distances. Thus in N cells of total volume $\cdot 65\,Na^3$ the change in the potential energy due to the changes in the distances between the titaniums and their six oxygen neighbours is

$$\tfrac{1}{2}\left[4N\,K_1\left(\frac{\cdot 438a}{n}\right)^2 + 8\,N\,K_1\left(\frac{\cdot 422a}{n}\right)^2 + 8\,N\,K_4\left(\frac{\cdot 325a}{n}\right)^2\right]$$

Proceeding in this way we get

$$\frac{9}{k} = \frac{1}{\cdot 65\,a^3}\left[4\,K_1\left(\cdot 191\,a^2 + \cdot 356\,a^2\right) + \right.$$
$$+ 2\,K_2\,(\cdot 288\,a^2) + 16\,K_3\,(\cdot 37\,a^2) +$$
$$\left. + 8\,K_4\,(\cdot 106\,a^2) + 8\,K_5\,(\cdot 606\,a^2)\right.$$

This gives us $K = \cdot 56 \times 10^{-12}$cm.^{2}/dyne which is almost the same as determined by Madelung and Fuchs (1921) which is $\cdot 58 \times 10^{-12}$cm.^{2}/dyne.

The above investigation was carried out in the Indian Institute of Science, Bangalore, during the summer vacations of 1950, at the instance of Sir C. V. Raman and Dr. R. S. Krishnan, to both of whom the author expresses his thanks for the interest shown in the work.

The author, also wishes to express his thanks to the U.P. Government for a grant.

Summary

The vibration specturm of Rutile has been studied by group theoretical methods. It has been shown that the structure possesses eleven frequencies. four of which are active in the Raman effect, six in the infra-red and one is inactive in both. The numerical values of the frequencies have been worked out on the basis of four empirically assumed force constants. It is found that there is a fair agreement between the observed values of the infra-red reflection maxima and the calculated values. The observed and calculated values of the compressibility also agree well.

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MAGNETIC SUSCEPTIBILITY OF THE CH_2 GROUP IN A HOMOLOGOUS SERIES OF ALIPHATIC ORGANIC ACIDS AND THEIR ALKALI AND ALKALINE EARTH SALTS

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The literature reveals that the values for χ_{CH_2} deduced from several homologous series vary from 11·87 to 11·36 (*cf.* Table I) (All values of the susceptibilities in this paper have been expressed in the units of -1×10^{-6}c.g.s.). This leads one to conclude that the value of χ_{CH_2} may not be a fixed quantity but may vary with the homologous series. Actually, Angus and Hill[2] have observed that the substitution of a methyl group in an acid lowers the value of χ_{CH_2} by 1·0. It is, however, not possible to ascertain how far these differences are significant.

In this paper, the authors have examined the data obtained by them on the susceptibilities of some aliphatic acids and their alkali and alkaline earth salts with a view to find the susceptibility of the $> CH_2$ group.

Table I

Investigator	χ_{CH_2}	Series investigated
Pascal ..	12·35 Uncorrected 11·86 Corrected	Alcohols, aldehydes, ketones, acids and amines
Bhatnagar, Mitra and Tuli[1]	11·36	Aliphatic alcohols, acids, esters and aromatic hydro-carbons
Angus and Hill[2] ..	11·68	Alcohols, acids, esters, aromatic hydro-carbons and esters
Bhatnagar and Mitra[3] ..	11·68	Alcohols, acids, hydro-carbons, aliphatic and aromatic aldehydes, ketones, esters, halogen derivatives, nitrogenous compounds and acetylinic compounds
Cabrera and Fahlenbrach[4]	11·48	Alcohols
Woodbridge[5] ..	11·67	Acetic acid and alkyl acetates
Gray and Cruickshank[6] ..	11·87	Organic nitrates, nitrites and nitro-compounds
Farquharson and Sastri[7] ..	11·64	Normal aliphatic acids

Experimental

All the compounds used in this investigation were chemically pure. Their magnetic susceptibilities were measured on a modified form of Gouy's balance by the method adopted by Prasad, Dharmatti and Gokhale[8] using KCl (A.R. quality) as standard substance. The results obtained are a mean of six independent readings.

Results

The observed magnetic susceptibilities of the compounds are given in Table II in which the following notations have been used:—

χ_a = specific susceptibility.

χ_m = molecular susceptibility.

χ_{ma} = molecular susceptibility of anhydrous substance.

The values of χ_m and χ_{ma} have been given one below the other. Wherever hydrated substances have been studied, the molar susceptibility of the anhydrous salt has been calculated by subtracting the susceptibility of the molecules of water of crystallisation from the molecular susceptibility of the hydrate, assuming strict additivity.

Table II

Substance	χ_a	χ_m and χ_{ma}
Formic acid ..	0·434	20·00
Acetic acid ..	0·535	32·10
Propionic acid ..	0·578	42·80
Butyric acid ..	0·636	56·00
Palmitic acid ..	0·772	197·80
Stearic acid ..	0·771	219·40
Lithium formate, $1H_2O$ ..	0·494	34·57
		21·61
,, acetate ..	0·533	35·20
,, propionate ..	0·573	45·90
,, butyrate ..	0·608	57·20
,, palmitate ..	0·730	191·40
,, stearate ..	0·721	209·10
Sodium formate ..	0·360	24·50
,, acetate, $3H_2O$ ..	0·574	78·10
		39·22
,, propionate ..	0·509	48·90
,, butyrate ..	0·560	61·60
,, palmitate ..	0·706	196·40
,, stearate ..	0·729	223·10

TABLE II—(*Contd.*)

Substance	χ_a	χ_m and χ_{ma}
Potassium formate* ..	0·370	31·10
,, acetate* ..	0·454	44·60
,, propionate* ..	0·510	57·20
,, butyrate* ..	0·555	70·00
,, palmitate ..	0·700	205·90
,, stearate ..	0·720	232·30
Magnesium formate, $2H_2O$ ..	0·464	69·74 43·82
,, acetate, $4H_2O$ ..	0·567	116·20 64·36
,, propionate, $1H_2O$ ..	0·527	99·30 86·34
,, butyrate ..	0·558	110·60
,, palmitate ..	0·705	376·80
,, stearate ..	0·718	423·90
Zinc formate, $2H_2O$ ..	0·400	76·63 50·71
,, acetate, $2H_2O$ ..	0·460	100·90 74·98
,, propionate ..	0·470	99·40
,, butyrate .	0·499	119·50
,, palmitate ..	0·673	387·00
,, stearate ..	0·692	436·60
Cadmium formate, $2H_2O$ ..	0·336	80·90 54·98
,, acetate ..	0·363	83·66
,, propionate ..	0·437	109·30
,, butyrate, H_2O ..	0·473	144·00 131·04
,, palmitate ..	0·645	401·60
,, stearate ..	0·650	440·60
Calcium formate ..	0·348	45·30
,, acetate ..	0·433	68·40
,, propionate ..	0·539	100·40
,, butyrate ..	0·558	119·45
,, palmitate ..	0·707	389·10
,, stearate ..	0·721	436·70
Strontium formate ..	0·339	60·30
,, acetate, ½ H_2O ..	0·318	87·70 81·22
,, propionate ..	0·462	107·90
,, butyrate, H_2O ..	0·510	142·60 129·64
,, palmitate ..	0·675	403·30
,, stearate ..	0·677	444·00
Barium formate ..	0·325	73·70
,, acetate ..	0·390	99·49
,, propionate, $1H_2O$ ..	0·453	136·50 123·54
,, butyrate ..	0·468	145·60
,, palmitate ..	0·645	417·40
,, stearate ..	0·654	459·95

* These salts being hygroscopic, their susceptibilities have been measured in solution.

Discussion of Results

Evaluation of χ_{CH_2}.—Pascal's method consists in subtracting the molecular susceptibility of a compound from that of its next higher homologue and then averaging all the values thus obtained for the series concerned. It is obvious that in such a case the accuracy of χ_{CH_2} would depend on the purity of first and the last members of the series.

Farquharson and Sastri[7] plotted χ_m of compounds belonging to a homologous series against n the number of CH_2 groups in the molecule, subtracted the intercept of the straight line on the χ_m axis from the molecular susceptibility of each member of the series, and therefrom calculated the average value of χ_{CH_2}. The same method has been adopted by Angus and Hill.[2] This method has an advantage over that of Pascal's as it utilises the observed molar susceptibility of each member of the homologous series.

The present authors, however, consider that the value of χ_{CH_2} should be calculated from the slope of the $\chi_m - n$ straight lines as it will be free from small errors involved in the actual measurements of the molecular susceptibilities of individual compounds which are smoothened out in drawing the straight lines. The authors have, therefore, plotted the graphs of the molecular susceptibilities of (*i*) the aliphatic fatty acids and (*ii*) the Ca, Sr, Ba, Mg, Zn, Cd, Li, Na and K salts of these acids against the number of CH_2 groups in the molecules. These are shown in Fig. 1.

The values of χ_{CH_2} calculated from each straight line are given in Table III. It will be seen from the table that (*i*) the value of χ_{CH_2} obtained from the series of acid agrees quite well with those reported by Bhatnagar and Mitra and Angus and Hill (*cf.* Table I), and (*ii*) the values of χ_{CH_2} obtained from different series may be different.

Table III

Series	χ_{CH_2}
Acids ..	11·83
Lithium salts ..	11·06
Sodium salts ..	11·50
Potassium salts ..	11·78
Magnesium salts ..	11·17
Zinc salts ..	11·30
Cadmium salts ..	11·36
Calcium salts ..	11·56
Strontium salts ..	11·42
Barium salts ..	11·47

In a recent publication, Mll. K. Kadomtzeff[9] has determined the susceptibilities of some plumbanes and has calculated the values of χ_{Pb} from these

compounds. The paper does not give the actual molar susceptibilities of these compounds but merely records the values of χ_{Pb}. Presuming *that values of χ_{Pb} were calculated by deducting the corrected data of Pascal for the susceptibilities of C and H from the observed molar susceptibilities of the plumbanes, the present authors have calculated the molar susceptibilities of these compounds and have plotted them against the number of CH_2 groups. The plotted points definitely lie on a straight line. The value of χ_{CH_2} calculated from the slope of the straight line is 10·8 which is again different from the values obtained from the homologous series of the acids and the alkali and alkaline earth salts. This observation lends further support to the conclusion that the value of χ_{CH_2} is specific for a given homologous series.

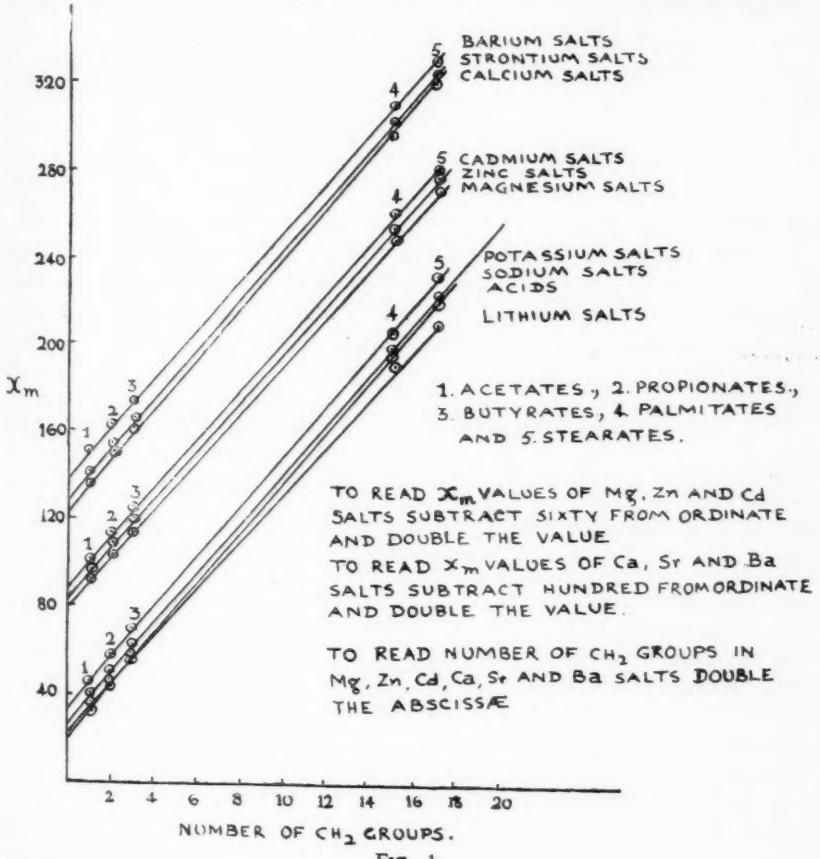
BARIUM SALTS
STRONTIUM SALTS
CALCIUM SALTS
CADMIUM SALTS
ZINC SALTS
MAGNESIUM SALTS
POTASSIUM SALTS
SODIUM SALTS
ACIDS
LITHIUM SALTS
1. ACETATES, 2. PROPIONATES,
3. BUTYRATES, 4. PALMITATES
AND 5. STEARATES.
TO READ χ_m VALUES OF Mg, Zn AND Cd SALTS SUBTRACT SIXTY FROM ORDINATE AND DOUBLE THE VALUE
TO READ χ_m VALUES OF Ca, Sr AND Ba SALTS SUBTRACT HUNDRED FROM ORDINATE AND DOUBLE THE VALUE.
TO READ NUMBER OF CH_2 GROUPS IN Mg, Zn, Cd, Ca, Sr AND Ba SALTS DOUBLE THE ABSCISSÆ
χ_m
320
280
240
200
160
120
80
40
2 4 6 8 10 12 14 16 18 20
NUMBER OF CH_2 GROUPS.

FIG. 1

* This presumption has been confirmed from Mll. Kadomtzeff in a private communication.

The values of the intercepts of the straight lines shown in Fig. 1 have been read and given in Column 2 of Table IV. They should represent the susceptibilities of formic acid and of the metal formates. Hence, these values have been compared with the observed values of formic acid and metal formates studied by the authors. The two values agree well with each other in most cases.

TABLE IV

End group in the homologous series	χ_m	
	(from the graph)	(Observed)
Formic acid ..	20·0	20·0
Lithium formate ..	22·0	21·61
Sodium formate ..	26·0	24·50
Potassium formate ..	32·0	31·10
Magnesium formate ..	42·0	43·82
Zinc formate .	50·0	50·71
Cadmium formate ..	59·0	54·98
Calcium formate ..	44·0	45·30
Strontium formate ..	59·0	60·30
Barium formate ..	74·0	73·70

This confirms that (*i*) the relation between χ_m and n for a homologous series is definitely linear, (*ii*) the susceptibilities of the CH_2 group and the rest of the molecule of a particular homologous series is definitely additive, and (*iii*) probably the value of χ_{CH_2} is definite only for the $> CH_2$ group in the molecules of a given homologous series.

SUMMARY

The susceptibility of CH_2 group has been determined from the molecular susceptibilities of a homologous series of aliphatic acids and their alkali and alkaline earth salts. It has been found that the value of χ_{CH_2} is constant for a given homologous series but may be different for different series.

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ACCELERATED OXIDATION OF COTTON CELLULOSE IN PRESENCE OF REDUCING SUBSTANCES—PART II

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Introduction

In the previous communication,[1] an account of the measurements of oxidation potentials of dilute sodium hypochlorite solutions and of the estimation of oxygen consumption from such solutions when cotton dyed with reduced Cibanone Orange R was treated with them, was given. It was shown that the curves relating "corrected oxidation potential" to pH and oxygen consumption to pH, were similar in shape at 20° C., but at 30° C. the shapes of the curves showing this relationships were not at all comparable. It was suggested that the method of applying correction to the measured oxidation potential at 20° C. was either not applicable to similar measurements at 30° C. or that the oxidation potentials were not at all indicative of the intensity of oxidation.

Nabar and Turner[2] made earlier similar observations by replacing the accelerating system leuco vat dye→vat dye by ferrous hydroxide→ ferric hydroxide. They showed that at 20° C. the oxidation of cellulose in the presence of ferrous hydroxide resembled in principle, the oxidation of cellulose accelerated by leuco Cibanone Orange R, but the pH for maximum oxygen transfer and for maximum cuprammonium fluidity of the oxidised cotton in presence of ferrous hydroxide was shifted approximately by one pH unit to the acid side from the region of maximum activity in presence of reduced Cibanone Orange R.[3] Apart from these differences, however, the reaction accelerated by ferrous hydroxide appeared to be similar to that accelerated by a reduced vat dye. Their results further indicated a fairly consistent mode of oxygen transfer to cellulose over the whole pH range a fact which was strongly demonstrated by earlier results with leuco Cibanone Orange R.[3] It is of great interest to point out that only the pH for maximum oxygen transfer to cellulose from sodium hypochlorite solution is influenced by the reduced substance deposited on the fibre, but the mechanism of oxidation of cellulose remained unaltered. These results further indicated that the method of correcting the measured oxidation potentials to explain the shape of the pH-oxygen uptake curve, is not applicable to all accelerated oxidation systems even at 20° C.; otherwise the difference in the pH for

maximum oxygen transfer in presence of the above two reducing substances would not have occurred.

From the foregoing it may be concluded that the rate of oxygen transfer to cellulose during hypochlorite treatment is primarily conditioned by the physico-chemical behaviour of the reducing substance present on the cellulose substrate. The present investigation was undertaken to see how far the behaviour of reducing substances of varied chemical structure, substantiated the above conclusion. From a study of the behaviour of twelve leuco vat dyes belonging to widely differing chemical structure, it is shown that the shape of the curve relating pH to oxygen uptake is not at all comparable with the pH-corrected oxidation potential curve. Further, the pH for maximum oxygen transfer is entirely determined by the particular reducing substance present on the cellulose.

These results fully substantiate the suggestion[1] that the corrected oxidation potentials obtained by applying $\cdot 06 \times$ pH volts (30° C.) as correction to the measured value of the potential is not indicative of the oxidising intensity of hypochlorite solutions.

Experimental Methods

Cotton.—Grey yarn (18's) manufactured from Indian cotton was carefully purified by subjecting it to a standard bleaching treatment. In the fully bleached condition, the cellulose possessed the following chemical properties: Cuprammonium fluidity[4] (0·5% solution) = 3·7; copper number[5] = 0·015; milliequivalents of $-COOH$ per 100 g. cellulose[6] = 0·5.

About 50 g. of the purified yarn was dyed with each of the vat dyes as described in the earlier communication.[3] The dyed yarn was conditioned. For each hypochlorite treatment $10 \pm 0 \cdot 1$ g. of the conditioned yarn was used. It was reduced using 2% cold sodium hydrosulphite solution and after repeated washing with oxygen-free distilled water to remove sodium hydrosulphite, the reduced dyeing was treated with sodium hypochlorite solution adjusted to a definite hydrogen-ion concentration and strength of available chlorine. The details of the reduction, the hypochlorite treatment and the determination of the oxygen consumed are similar to those used by Nabar, Scholefield and Turner.[3]

Application of ferrous hydroxide to yarn and determination of oxygen consumed by ferrous hydroxide deposited cotton when treated with sodium hypochlorite solutions.—The production of cotton uniformly impregnated with the desired hydroxide and of approximately constant iron content was carried out as follows: Skeins of cotton (5 g.; 54 in. circumference) were cut through at one point. A tight tie-band was placed at each cut end, as near

to the end as possible. The whole was weighed, placed in a 600 ml. beaker and covered with 400 ml. of a solution of ferrous ammonium sulphate containing 195 g. A. R. $FeSO_4.(NH_4)_2SO_4.6H_2O$ and 5 ml. of 5-N-sulphuric acid in 1 l. of boiled-out water. After uniform agitation the cotton was allowed to stand for 4 min. under the surface of the solution. It was then opened out and passed in the rope-like form at a fixed uniform speed through a pad mangle with rubber-rollers. By fixing a mark on the screw adjusting the roller pressure, and bringing the screw always to the same position, each batch of cotton was submitted to approximately the same pressure during padding, and it was found that the expression of liquid varied very little from one batch of cotton to another. After one padding, the cotton was again immersed in the iron solution, after it had been brought up to its original volume by adding fresh stock solution. The padding operation was repeated and the yarn transferred to 500 ml. of N-sodium carbonate solution prepared with cold, boiled out distilled water. It was stirred continuously under the surface for 1 min. and allowed to stand for a further 2 min. Stirring in this way is essential to ensure uniform distribution of the precipitate on the fibre. After precipitation of the hydroxide, the yarn was removed from the alkali solution, squeezed rapidly and washed under the surface of a large volume of cold, boiled out distilled water. The washing treatment was repeated 5 times, and the yarn then squeezed rapidly and uniformly and transferred at once to the appropriate buffered hypochlorite solution. The ferrous hydroxide precipitated in this way was pale and rather dull green.

The yarn thus obtained was immediately transferred to a suitably buffered sodium hypochlorite solution and the loss of available oxygen was determined after 10 min. treatment. The details of the procedure are similar to those described by Nabar and Turner.[2]

Determination of cuprammonium fluidity.—The curpammonium fluidity of the various oxidised samples was determined by the method of Clibbens and Geake.[4] Owing to the high level of degradation of most of the samples, the fluidity was determined in 1% solution.

Determination of copper number.—The copper number has been determined by Hayes' micro-method.[5] Due to the high level of degradation, half the weight of sample, normally recommended, has been taken. Another noteworthy feature is that N/25 potassium permanganate solution is replaced by N/25 ceric sulphate using *o*-ferrous phenanthroline complex as internal indicator.

Determination of carboxyl content.—The determination has been carried out by Neale and Stringfellow's alkali titration method.[6] One gram of the

cation-free material is suspended in a mixture of 25 ml. of carbonate free 0·02 N caustic soda, 25 ml. of 5% solution of sodium chloride and 25 ml. of carbon dioxide-free distilled water. At the end of one hour the excess of alkali is back titrated with 0·02 N hydrochloric acid using Bromo-Cresol purple as indicator.

Estimation of iron on the fibre.—About 1 g. of the cotton was slowly ignited in a platinum crucible and heated for three hours. At the end it was cooled and digested with concentrated hydrochloric acid. The solution was then transferred to a conical flask and the crucible washed with 2 N hydrochloric acid. The contents of the flask were then diluted with dilute hydrochloric acid, 10 ml. of concentrated hydrochloric acid added and heated to boiling. Stannous chloride solution (3%) was then added drop by drop till all the iron was reduced. To the cold solution, 10 ml. of mercuric chloride and a drop of ortho-ferrous phenanthroline was added and the solution titrated against N/50 ceric sulphate.

Experimental Results

A synopsis of experimental results is given in Tables I to III. From a study of twelve vat dyes of widely differing chemical structure, it is found

Table I. *Oxidation of cellulose in presence of leuco compounds of vat dyes (30°C.) for ten minutes*

pH of hypochlorite solution	Cibanone Orange R		Cibanone Yellow R		Indathrene Yellow FFRK		Indanthrene Yellow G		Ciba Green G	Cibanone Yellow GC	Caledon Gold Orange G
	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(A)	(A)
5·0	10·0	13·3	..	..	9·0	12·9	13·8	18·0	15·8	..	..
5·1	..	..	8·2	9·8	..	..	..	..	..	11·1	8·0
5·5	..	..	..	..	..	..	..	..	..	13·3	..
5·8	..	..	..	..	..	..	15·8	23·6	..	..	..
6·0	16·0	23·7	..	..	11·2	15·8	16·7	29·4	..	..	10·5
6·1	16·9	25·9	12·2	15·8	..	..	..	..	19·9	15·7	..
6·5	..	..	14·8	22·5	11·4	16·7	..	..	..	18·4	13·0
7·	..	..	..	..	..	..	18·0	28·0	21·8	21·1	14·3
7·1	..	..	..	..	13·7	19·9	..	..	..	..	..
7·3	20·7	30·9	15·8	23·4	..	..	..	..	..	19·0	13·6
8·1	17·2	26·4	..	..	8·7	10·5	12·1	16·0	..	..	..
8·2	..	..	11·6	18·0	..	..	..	..	17·4	15·5	7·7
8·5	12·3	19·0	..	..	..	..	..	..	..	..	..
8·6	..	..	..	..	..	..	9·8	12·4	..	..	..
8·7	..	..	..	..	..	..	..	..	..	9·0	..
9·0	..	..	..	..	..	..	..	..	14·0	..	..
9·1	8·6	14·1	6·0	10·2	5·9	6·6	6·7	8·0	..	..	..
9·3	=	..	..	..	..	..	..	..	..	8·5	5·0

A = Milliatoms of oxygen consumed per 100 *g.* of reduced dyeing.
B = Cuprammonium fluidity of the treated dyeings (1% solution).

TABLE II. *Oxidation of cellulose in presence of leuco compounds of vat dyes (30° C.) for ten minutes*

pH of hypochlorite solution	Ciba Blue 2B		Ind. Dark Blue BO	Cal. Green BS	Cal. Jade Green XS
	A	B	A	A	A
4·5	..	..	28·7	22·5	12·0
4·6	22 8	24·5	30·0	..	..
5·1	..	..	..	..	14·0
5·4	27·8	27·5	33·6	25·2	15·8
5·8	31·8	31·0	..	..	..
6·0	..	..	..	21·6	..
6·1	..	..	22·2	..	12·0
6·3	34·4	34·5	..	..	..
6·5	..	..	..	15·1	10·8
6·7	..	..	12·7	..	..
7·0	..	..	11·5	13·2	..
7·3	28·4	21·6	..	..	..
7·6	..	..	..	..	8·0
8·0	24·8	13·1	..	..	..
8·2	..	..	7·9	10·6	7·4
9·0	20·6	11·0	7·0	..	..
9·2	..	..	..	9·6	7·4

A = Milliatoms of oxygen consumed per 100 grams dyeing.
B = Cuprammonium fluidity of the treated dyeing (1% solution).

TABLE III. *Oxidation of cotton impregnated with ferrous hydroxide (30°C.) for ten min.*

pH of hypochlorite solution	Per cent. of Fe on the fibre	Milli-atoms of oxygen per 100 g. of cotton	Cuprammonium fluidity (1% solution)	Increase in copper number	Increase in -COOH m.e. per 100 g. of Cotton
5·4	1·18	31·1	28·2	8·2	5·0
6·8	1·14	33·1	29·5	3·3	5·2
6·3	1·22	39·0	32·3	9·6	6·2
6·7	1·13	33·1	30·1	8·5	5·2
7·0	1·15	22·0	25·3	5·7	3·6
7·4	1·22	16·1	21·2	4·3	2·5
8·0	1·23	5·7	10·0	0·8	1·3
9·1	1·21	2·2	1·3	0·1	0·7
10·0	1·21	1·14	0·9	0·04	0·5

that they fall into three categories with respect to their influence on the rate of oxygen transfer to cellulose. In Table I are given results obtained with seven dyes which may be said to show a normal behaviour, comparable with the known properties of hypochlorite solutions during bleaching practice.

The maximum oxygen transfer to cellulose takes place in this case at about pH 7·3. These results are shown in Fig. 1.

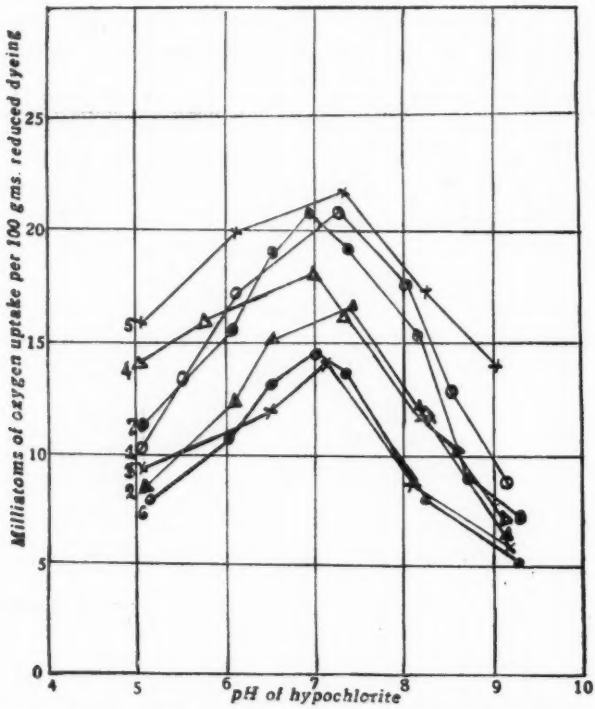

FIG. 1. Relation between pH and oxygen uptake by reduced dyeings of (1) Cibanone Orange R; (2) Cibanone Yellow R; (3) Indanthrene Yellow FFRK; (4) Indanthrene Yellow G; (5) Ciba Green G; (6) Caledon Gold Orange G; and (7) Cibanone Yellow GC, when treated with dilute sodium hypochlorite solutions for 10 mins.

It is seen that the general shape of the curves for the various dyes is similar to one another, only the intensity of oxidation is different.

In Table II results obtained with leuco Ciba Blue 2B, Indanthrene Dark Blue BO, Caledon Green BS and Caledon Jade Green XS are given. The maximum oxygen uptake with Ciba Blue 2B occurs at about pH 6·3, but with the other three dyes the same takes place at about pH 5·4. The relation between pH and oxygen uptake for these four dyes is shown in Fig. 2.

The results obtained when cotton impregnated with ferrous hydroxide was treated with hypochlorite solutions at 30° C. are given in Table III and

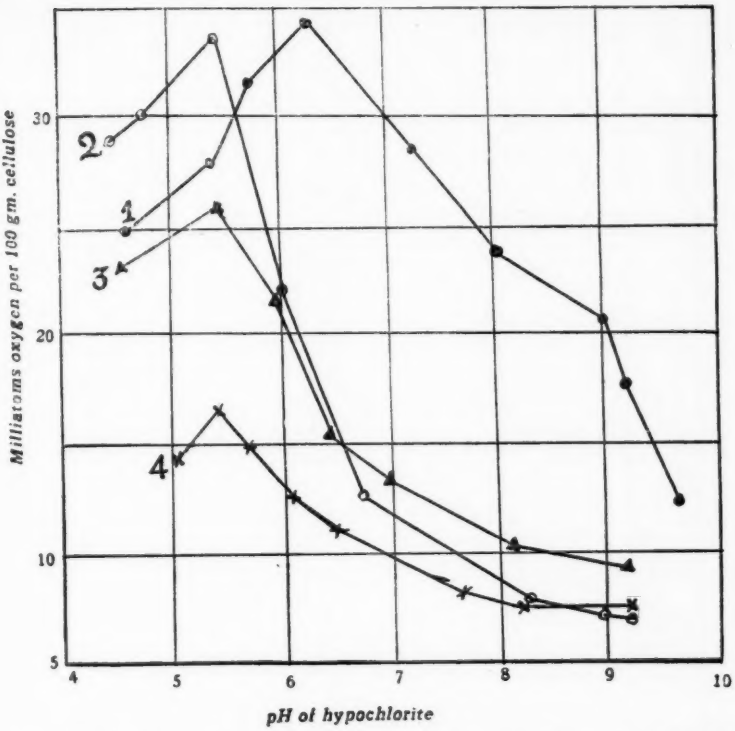

FIG. 2. Relation between pH and oxygen uptake by reduced dyeings of (1) Ciba Blue 2B; (2) Indanthrene Dark Blue BO; (3) Caledon Green BS; and (4) Caledon Jade Green XS when treated with dilute sodium hypochlorite solutions for 10 mins.

shown in Fig. 3. In this case the maximum oxygen transfer takes place at about pH 6·3. For ready reference similar curve at 20° C. reproduced from the paper by Nabar and Turner[2] is also shown in the same figure. The shape of the curves at 20°C. and 30°C. is similar. In the same figure curves relating pH to (*a*) cuprammonium fluidity, (*b*) copper number and (*c*) carboxylic acid content for the ferrous hydroxide oxycellulose samples at 30°C. are shown. The shape of these three curves is similar to the shape of the pH oxygen curves at 20° C. and 30° C. This indicates that the mechanism of oxidation is the same at both the temperatures.

In Fig. 4 the curves relating pH to corrected oxidation potentials both at 20° and 30° C. are reproduced from the earlier communication,[1] for ready

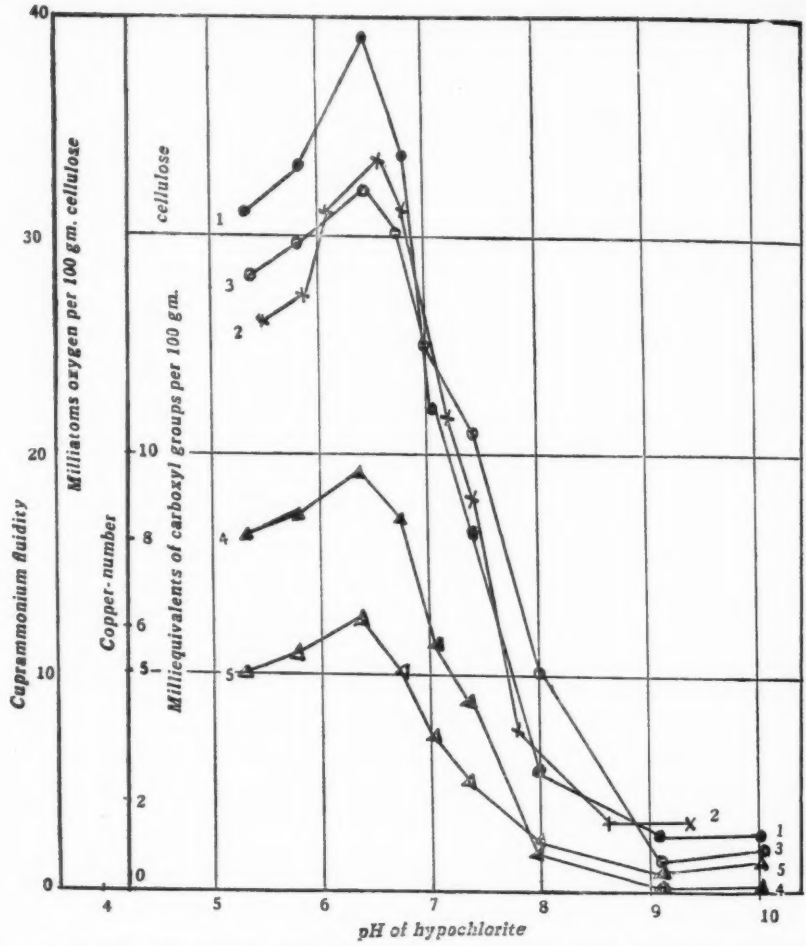

FIG. 3. Relation between pH and (1) Oxygen uptake (30° C.); (2) Oxygen uptake (20° C.) (3) Cuprammonium fluidity (30° C.); (4) Copper number (30° C.); (5) Carboxylic acid content (30° C.) for ferrous hydroxide impregnated cotton when treated with dilute sodium hypochlorite solutions for 10 mins.

reference. It is interesting to point out that the curves shown in Fig. 1 resemble in shape the curve relating pH to corrected oxidation potential at 20° C. but none of the curves in Figs. 1 to 3 show any resemblance to a similar curve (Fig. 4) at 30° C.

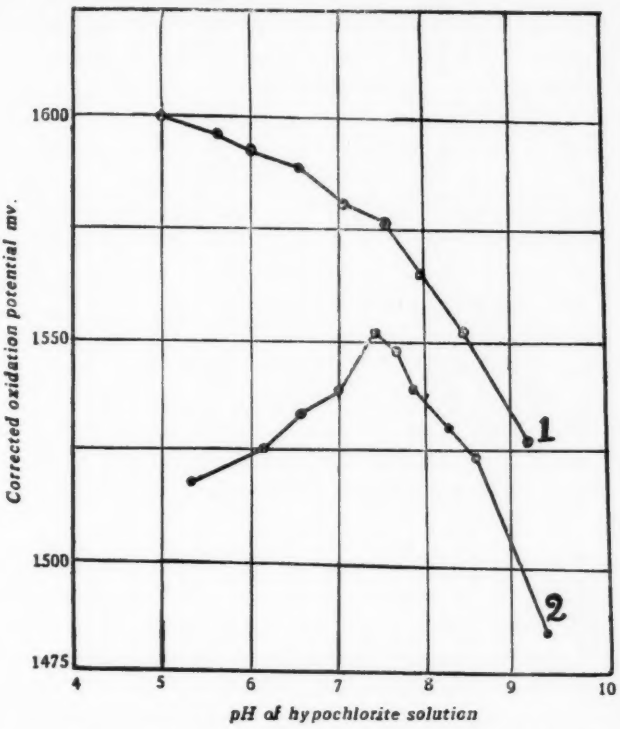

FIG. 4. Relation between pH and corrected oxidation potentials of sodium hypochlorite solutions at (1) 30° C. and (2) 20° C.

DISCUSSION

The curves in Figs. 1, 2 and 3 bring out the influence of reducing substances on the rate of oxygen transfer to cellulose from hypochlorite solutions in a striking manner. Although for each of the various dyes examined the similarity in shape of the curves relating pH to (*a*) oxygen consumed, (*b*) cuprammonium fluidity, (*c*) copper number and (*d*) carboxylic acid content does not materially alter, each accelerator is found to have its own influence on the degree of oxidation. Further, the oxidation, accelerated by leuco compounds of Cibanone Orange R, Cibanone Yellow R, Caledon Yellow GN, etc. shown in Fig. 1 shows a maximum intensity of oxidation between pH 7 and 7·3. By replacing the above accelerating systems by leuco Ciba Blue 2B, the maximum oxygen consumption is shifted to pH 6·3, while leuco compounds of Indanthrene Dark Blue BO, Caledon Green

BS and Caledon Jade Green XS cause the pH for maximum oxygen transfer to be shifted to 5·4. In presence of the inorganic accelerating system ferrous hydroxide → ferric hydroxide, the maximum oxygen transfer takes place at about pH 6·3. It is thus clear that the reducing substance present on the cellulose, maintains its identity. This is seen from the following *viz.*, the shift in the pH at which maximum oxygen transfer and maximum chemical attack on the cellulose substrate takes place. It appears that some intrinsic physico-chemical property of the reducing substance present on cellulose during the oxidation, is responsible for this behaviour.

Comparing these results with those for the corrected oxidation potentials in Fig. 4, it is found that the curve at 30° C. shows no resemblance to any of the curves relating pH to oxygen transfer in Figs. 1, 2 and 3. Hence no linear relationship between the corrected oxidation potentials and oxygen transfer may be expected. Nabar, Scholefield and Turner[3] obtained a linear relationship between these two quantities for leuco Cibanone Orange R at 20° C. But as will be seen from the results described earlier, this does not seem to be possible for leuco Cibanone Orange R at 30° C. or for ferrous hydroxide even at 20°C.

It must be pointed out here that the system leuco vat dye → vat dye is not as simple as it appears at first sight. This is further complicated by the influence of the hydrogen-ion concentration of the oxidising system as it profoundly affects the dissociation of the weakly acidic dissociable groups of the leuco compounds. Since the influence of the reduced vat dye on the oxidation is so considerable, it may be reasonably assumed that the physico-chemical properties of the leuco compound will influence the course of oxidation and also the rate of oxygen transfer to the cellulose substrate on which they are deposited. Electrical measurements on the system leuco vat dye → vat dye are extremely difficult to carry out owing to the very low solubility of these compounds in aqueous medium. Attempts are being made in this laboratory to study this aspect of the investigation.

Summary

1. The relation between pH of sodium hypochlorite solutions and the amount of oxygen consumed at 30° C. by cotton in presence of ferrous hydroxide and a number of vat dyes belonging to different chemical structural groups, is determined.

2. It is found that the reduced substances do not show uniform behaviour. The rate of oxygen uptake, the amount of oxygen transferred and the pH of maximum oxygen uptake by the cellulose substrate, are dependent

on the individual reducing substance present on the fibre during the hypochlorite treatment.

3. At 30° C., there exists no similarity between the pH-corrected oxidation potentials curve and the curve showing relation between pH and oxygen uptake or fluidity.

4. The corrected oxidation potentials as obtained by applying a correction of $0{\cdot}06 \times$ pH volts to the measured value of the potentials is not a measure of the oxidising intensity of hypochlorite solutions.

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KINETIC STUDIES IN ESTER HYDROLYSIS

Part V. The Influence of Solvent on the Reaction*

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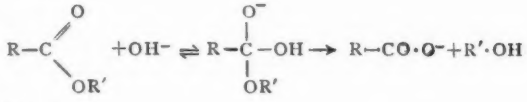
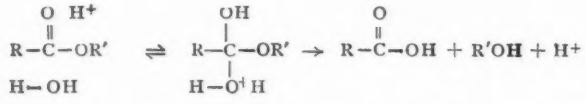
In Parts III and IV of this series the results of a study of the acid catalysed and alkaline hydrolysis of ethyl acetate in dioxane-water and acetone-water mixtures have been presented and a few observations made regarding the variation of velocity constant with changes in composition of the solvent. In this communication the influence of solvent and the light it throws on certain aspects of the mechanism of the reaction are more fully considered.

The mechanisms proposed by Davies and Evans[1] are made use of for the present discussion.

Alkaline Hydrolysis:



Acid Hydrolysis:



These mechanisms have been found to be as satisfactory as the original ones proposed by Lowry in the interpretation of substituent effects and they have got the additional advantage that they give a more satisfactory picture of the reaction.

Alkaline Hydrolysis

In the mechanism for alkaline hydrolysis given above, the water molecule, which is usually associated with it, is omitted since the initial and final stages of the reaction do not require or indicate the presence of water in the transition complex. The authors, however, do not neglect the water mole-

* Part of a thesis of P.M.N approved for the M.Sc. Degree of the Madras University.

cule entirely. They consider that the water molecule might possibly have a different function, namely, stabilisation of the transition complex. This picture of the reaction has not been widely accepted and use of the Lowry mechanism which postulates definite participation of the water molecule in the transition complex, is still quite frequent. The position remains uncertain since no clear proof has been provided either way.

It is easily seen that a consideration of the data provided by studies of the reaction in mixed solvents, where one component is water, is likely to throw some light on the doubtful role of the water molecule. The conflicting treatments of alkaline hydrolysis—the one treating it as between ion and dipole while the other considers it as a dipole-dipole reaction—and their respective experimental evidences have been already referred to in Part IV (this volume p. 187). The question that is to be settled, therefore, is whether the reaction is between ion and dipole or between dipole and dipole or whether it actually involves two dipoles and an ion. Putting it in terms of the species present, it has to be decided whether the reaction can be looked upon as between the hydroxyl ion and ester molecule or between ester and water molecules or if it requires the co-operation of all the three.

The reactants involved clearly show that in a consideration of the solvent effect we have got to deal primarily, with electrostatic forces. For a reaction between two dipoles the dependence of reaction velocity on the dielectric constant of the medium is given by the following equation[3,6]:

$$\ln k = \ln k_0 - \frac{1}{kT}\frac{D-1}{2D+1}\left(\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_\ddagger^2}{r_\ddagger^3}\right) + \frac{\Sigma\phi}{kT}$$

where the μ's are dipole moments of the reacting dipoles (A and B) and the activated complex, r's their respective radii and $\Sigma\phi$ is the correction term for non-electrostatic forces which are comparatively negligible. Therefore, $\ln k$ should vary linearly with $\frac{D-1}{2D+1}$ and in cases where the dipole moment ($\mu_\ddagger$) of the activated complex is large compared with those of the reactants, as is generally the case where the products are ions or are highly polar, the slope of the line will be positive. Curves 1 and 2 of Fig. 1 and Fig. 2 show the variation of log k with $\frac{D-1}{2D+1}$. Excepting curve No. 1 there is a maximum in each corresponding to the one observed in the case of velocity composition curves. The slopes of the curves right of the maxima clearly indicate that for solvent compositions corresponding to this region (*i.e.*, below 10% organic solvent) the reaction does not behave as one

between dipoles since it is absolutely impossible to visualise a change in sign for the expression,

$$\left(\frac{\mu_A^2}{r_A^3}+\frac{\mu_B^2}{r_B^3}-\frac{\mu_\ddagger^2}{r_\ddagger^3}\right).$$

Even for portions of the curves left of the maxima there is pronounced departure from linearity for the higher percentages of organic solvent. The linear correlation exists only within a limited range.

On the other hand, if the reaction is between ion and dipole, the variation of velocity with dielectric constant should conform to the equation[4,7]:

$$\ln k = \ln k_0 + \frac{e^2 z_A^2}{2kT}\left(\frac{1}{D}-1\right)\left(\frac{1}{r_A}-\frac{1}{r_\ddagger}\right) - \frac{1}{kT}\cdot\frac{\mu_B^2}{r_B^3}\cdot\frac{D_0-1}{2D_0+1} + \left(b_A - b_\ddagger + \frac{e^2\delta}{DrkT}\right)j + \frac{\Sigma\phi}{kT}$$

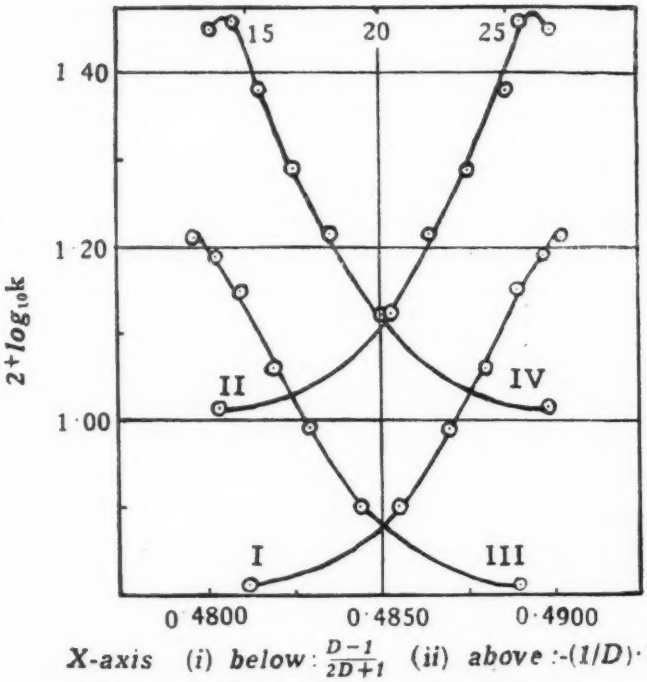


FIG. 1. Alkaline Hydrolysis in Acetone-Water Mixtures.

Curve No.	Temp.	
I	30°C.	Plots of $\frac{D-1}{2D+1}$ against log k
II	40°C.	
III	30°C.	Plots of $1/D$ against log k
IV	°	

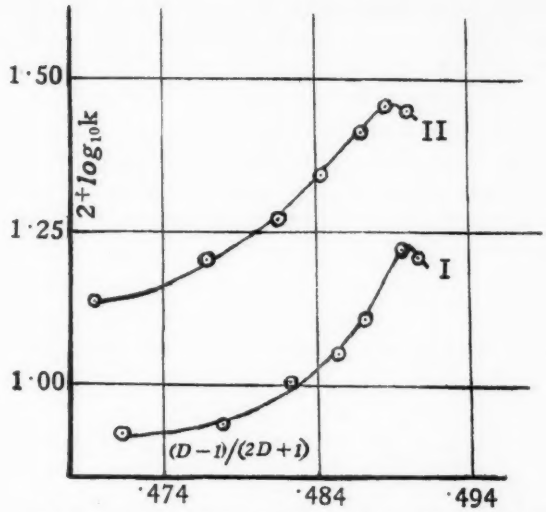


FIG. 2. Variation of log k with $(D-1)/(2D+1)$ for Alkaline Hydrolysis in Dioxane-Water Mixtures

Curve No. I II
Temp. 30°C. 40°C.

where e represents unit charge, z_A the charge of the ionic reactant A, μ_B the dipole-moment of reactant B, D_0 and D the dielectric constants of the pure solvent and the solution containing the non-electrolyte (*i.e.*, molecules of B), the r's the radii of A, B and the activated complex respectively and j the ionic strength of the solution. The bj terms represent the additional electrostatic terms due to Hückel and represents the Debye-McAulay correction for the change of dielectric constant due to the introduction of non-electrolyte and the $\Sigma\phi$ term the correction for non-electrostatic forces. An examination of the terms involved indicate that with a change of D, the changes in all of these will have the same effect on the rate constant. So, a decrease of dielectric constant should always increase the reaction velocity. Since for large values of D unity is negligible compared to $2D$, $\dfrac{D-1}{2D+1}$

$$\left[\text{which equals } \tfrac{1}{2}\left(1-\frac{3}{2D+1}\right)\right],$$

can be considered to be a linear function of $1/D$. Also the difference between D and D_0 is very small, as only dilute solutions are employed. Neglecting the Hückel terms and the Debye-McAulay and non-electrostatic correction terms which are of much smaller magnitude than the others, we should

therefore, find a linear relationship between *lnk* and $1/D$. Even though no values are available in the present investigation for compositions between zero and 10% organic solvent, the shapes of the curves obtained on plotting log k values against $1/D$ (only one representative curve is given in Fig. 1) leave no reason to doubt the existence of a linear variation within this range. However, the behaviour in acetone-water mixtures at 30° C. has to be considered exceptional (Curve I, Fig. 1), as has been noted in Part IV, until values for compositions intermediate between zero and 10% acetone are available.

The foregoing considerations, while making it clear that the transition in the trend of the velocity constants is due to some important factor concerning the reaction mechanism, do not give us any definite indication about it excepting that the water molecule is involved in some way. But, the mere numerical reduction of water molecules cannot be assumed to effect the reversal of the trend of k-values, because in 10% dioxane or acetone, water molecules are still present in an overwhelming proportion compared to the concentration of the reactants. Also, the fall of the velocity constants is much steeper than would correspond to a hidden molecularity with respect to water. Therefore, the reason for the observed change has to be sought elsewhere.

Soper and co-workers[8,9], in order to explain the marked solvent effects noticed in certain cases, have postulated that solvents may exert considerable influence on the fraction of activated complexes which break down to form reaction products. The decomposition into products is governed by the relative thermodynamic probabilities of the activated complex and the products respectively. Viewing it from the standpoint of the theory of absolute reaction rates this means that the transmission coefficient, κ, of the reaction rate equation,

$$k = \kappa \cdot \frac{kT}{h} e^{-\Delta F_t^{\ddagger}/RT}$$

is affected by solvents. A satisfactory interpretation of the behabiour of the rate constants is possible in the light of the ideas considred above. Progressive reduction of the water content of the medium results in a decrease of the transmission coefficient. The initial rise of the reaction velocity with increasing amounts of organic solvent in solution is attributable to the usual effect of decreasing dielectric constant on an ion-dipole reaction. But, as more and more of water is replaced by organic solvents, the effect of decreasing transmission coefficient overtakes the effect of the change in dielectric constant and the reaction velocities begin to fall.

As for the question about the extent to which the water molecule participates in the reaction, it has to be considered, in the light of the facts that have been discussed, as having an important part. But, its participation in the activated complex has to be ruled out since it has been shown conclusively by Jenkins[5] that changes in activation energies due to substituents can be accounted for quantitatively by the changes in the energy required to bring the hydroxyl ion to the carboxyl carbon atom. If the water molecule had been involved in the transition complex considerable portion of the activation energy would have been required to bring it to the reaction centre and changes in this amount would have also contributed to variations in energy of activation when substituents are altered. Therefore, it would be most reasonable to describe its role as the stabilization of the activated complex, thus increasing its chance of decomposition into the products of reaction.

The pronounced decrease in the rate of fall of velocity constants for the higher compositions of organic solvent has been already referred to. This behaviour must be due to the fact that the effect of non-electrostatic forces becomes quite considerable as we approach the limiting dioxane percentage beyond which separation into layers takes place in presence of alkali. Specific solvent influences are also seen to be at work from the difference noticed between the two solvent series in the variation of *k*-values with dielectric constant. As in the case of acid hydrolysis, the values obtained indicate that the *k*-values are more sensitive to changes in dielectric constant in acetone water mixtures than in dioxane-water mixtures.

Acid Hydrolysis

The position with regard to acid hydrolysis is less complicated. Since an experimental verification of the hidden molecularity with respect to water, which is usually assumed, has been achieved[2], the reaction must essentially be considered as termolecular. The activation energy for the reaction can, therefore, be considered to be composed of two parts, one for the polarisation of C = O bond and association of H^+ ion at the carbonyl oxygen and the other required for overcoming the forces of repulsion to bring the water molecule to the carbon atom. Since the carbonyl oxygen atom of the ester molecule is already fractionally negative owing to resonance between the two structures, $R-C\langle^{O}_{OR'}$, and $R-C\langle^{O^-}_{O^+R'}$ the energy required for the association of the proton will be very small in comparison with that required for the water molecule. Hence, the reaction can be expected to behave as one between dipoles. Figs. 3 and 4 give the plots of log *k* against

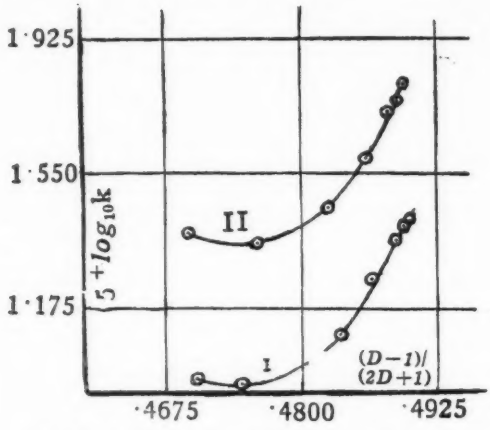


FIG. 3. Variation of log k with $(D-1)/(2D+1)$ for Acid Hydrolysis in Acetone-Water Mixtures.

Curve No. I II
Temp. 35°C. 45°C.

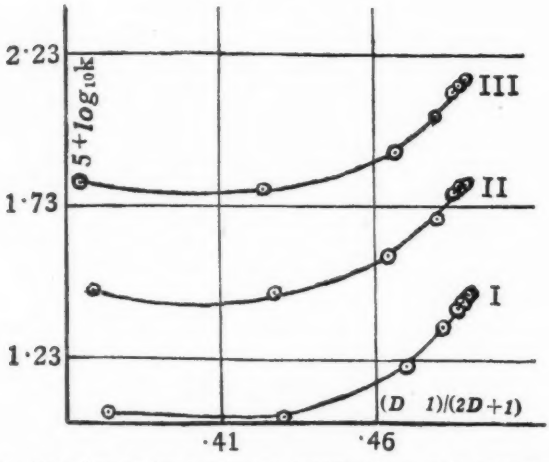


FIG. 4. Variation of log k with $(D-1)/(2D+1)$ for Acid Hydrolysis in Dioxane-Water Mixtures

Curve No. I II III
Temp. 35°C. 45°C. 55°C.

$\frac{D-1}{2D+1}$ for both dioxane-water and acetone-water mixtures. The first five points in each curve fall more or less on a straight line, *i.e.*, till 60% organic

solvent is reached. But, beyond this composition the fall in velocity becomes less and less and finally the curves flatten out, there being a slight rise in log k from 80% to 90% organic solvent. This is a clear indication that van der Waals forces come into play in media containing high percentages of organic solvent. The difference in internal pressures of the activated complex and the solvent becomes smaller compared with the differences between those of the reactants and the solvent, thus tending to increase the velocity and accounting for the slower fall of the rate constants, the flattening of the curves and the final small increase in velocity.

Summary

The influence of solvent on the rates of acid catalysed and alkaline hydrolysis of ethyl acetate has been discussed, the main factor taken into consideration being dielectric constant of the medium. Considerable light has been thrown on the precise role of the water molecule in alkaline hydrolysis. Specific solvent effects are also clearly noticeable since the reaction velocities, for both acid and alkaline hydrolysis, are more sensitive to changes in dielectric constant in acetone-water than in dioxane-water mixtures.

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KINETIC STUDIES IN ESTER HYDROLYSIS

Part VI. The Steric Factor in Ester Hydrolysis

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Received May 23, 1950

(Communicated by Dr. S. V. Anantakrishnan, F.A.SC.)

In many reactions, particularly in solution, low values have been observed for the frequency factor and amongst several explanations offered one is that of steric factor. Any reaction involves the breaking of a few bonds and the formation of new ones and encounters must necessarily be only in the region of the reaction centre to be effective. In the case of bromine addition to olefines[1] it has been observed that to a considerable extent the large difference between observed and calculated values of the frequency factor can be satisfactorily accounted for by the assumption that only encounters in the region of the double bond are effective. An approximate calculation of the correction factor has been made for this reaction and it was found that this could bring down considerably the enormous discrepancies between the observed and calculated frequency factors. A more rigid calculation of the steric correction factor is here made in the case of ester hydrolysis. For evaluating the steric factor, however, one has to take into account the exact mechanism of the reaction. The mechanisms of acid and alkaline hydrolysis of esters have been elucidated sufficiently clearly to permit calculations of the kind adopted here. The mechanisms proposed by Davies and Evans[2] have been used for the present communication.

Acid hydrolysis can be taken to involve two stages: the association of the proton (actually the hydronium ion is involved in the collision) with the ketonic oxygen and the encounter of a water molecule at the carbonyl carbon, followed by the decomposition of the transition complex. If the probability of the two stages be P_1 and P_2 respectively, assuming a value of unity for the transmission coefficient, the probability of chemical transformation will be P_1P_2. Due to the smallness of the hydronium ion and the water molecule, their orientations during collisions may be neglected without serious error. Since it is only the two lone pairs of electrons of the oxygen atom have to be reckoned for the primary encounter, the probability P_1 can be taken as approximately the ratio of half the surface area of the oxygen atom to the total surface area of the whole molecule and similarly P_2 will be

the ratio of the surface area corresponding to a pair of shared electrons of the carbon atom to the total surface area. (Since the first step converts C=O into C—O, we take the former as $\frac{1}{4}$ the surface area of carbon.) In calculating the surface areas of the ester molecules, aliphatic compounds were treated as cylinders while the benzene ring is treated as a hexagonal prism whose height is given by the diameter of a carbon atom. Radii of neutral atoms have been taken from the calculations of Hartree quoted by Slater[7] and values for bond angles and lengths from Pauling[6] and Wheland.[9] The results for both acid and alkaline hydrolysis are given below in Tables I–IV.

TABLE I

Acid Hydrolysis of Aliphatic Esters

Ester	Log Z calc.	Log P calc.	Log PZ calc.	Log PZ obs.[2]
Ethyl acetate ..	11·48	$\bar{4}$·56	8·04	7·53
,, propionate ..	11·58	$\bar{4}$·44	8·02	7·46
,, butyrate ..	11·67	$\bar{4}$·34	8·01	7·11
,, valerate ..	11·75	$\bar{4}$·25	8·00	7·35
,, hexoate ..	11·32	$\bar{4}$ 17	7·99	7·13
,, heptoate ..	11·89	$\bar{4}$·09	7·98	7·11
,, octoate ..	11·96	$\bar{4}$·02	7·98	7·16

TABLE II

Acid Hydrolysis of Aromatic Esters

Ester	Log Z calc.	Log P calc.	Log PZ cal.	Log PZ obs.[5]
Ethyl benzoate ..	11·72	$\bar{4}$·72	7·88	7·84
,, *p*-toluate ..	11·75	$\bar{4}$·12	7·87	7·88
,, anisate ..	11·84	$\bar{4}$·09	7·93	8·07
,, *p*-hydroxy benzoate ..	11·74	$\bar{4}$·13	7·87	7·83
,, *p*-chlorobenzoate ..	11·78	$\bar{4}$·13	7·91	7·77
,, *p*-bromo-benzoate ..	11·79	$\bar{4}$·12	7·91	7·72
,, *p*-Nitrobenzoate ..	11·75	$\bar{4}$·13	7·88	7·57
,, *m*-nitrobenzoate ..	11·72	$\bar{4}$·13	7·84	7·73

TABLE III

Alkaline Hydrolysis of Aliphatic Esters

Ester	Log Z calc.	Log P calc.	Log PZ cal.	Log PZ obs.[3]
Ethyl acetate ..	11·51	$\bar{4}$·51	8·07	5·90
,, propionate ..	11·61	$\bar{4}$·44	8·05	6·10
,, butyrate ..	11·70	$\bar{4}$·34	8·01	6·50
,, valerate ..	11·78	$\bar{4}$·25	8·03	6·90
,, heptoate ..	11·92	$\bar{4}$·09	8·01	6·90

TABLE IV

Alkaline Hydrolysis of Aromatic Esters

Ester	Log Z calc.	Log P calc.	Log PZ cal.	Log PZ obs.[4]
Ethyl benzoate ..	11·70	$\bar{4}$·16	7·87	7·67
,, anisate ..	11·82	$\bar{4}$·09	7·91	8·17
,, *p*-nitrobenzoate .	11·73	$\bar{4}$·13	7·86	8·66
,, *m*-nitrobenzoate ..	11·70	$\bar{4}$·13	7·83	8·66

The agreement between the calculated and experimental values in the case of acid hydrolysis (Tables I and II) is very close indeed and the somewhat larger difference noticed in the case of aliphatic esters may be in part at least due to small inaccuracies in the values of collision diameters arising from the flexibility of the long chains. In the case of alkaline hydrolysis, while the agreement is satisfactory for aromatic esters (Table IV), the differences are somewhat larger for aliphatic ones particularly the earlier members. But, it should be noted that there are complicating factors at work in the case of aliphatic esters. Activation energy is lowered abnormally, especially for the lower homologues and since the PZ factors have a tendency to follow changes in activation energy, these are also depressed by a corresponding amount. However, even in these cases, it is clear that the correction introduced covers the greater part of the gap between the ' normal ' and experimental values of the frequecy factor.

The reaction rate equation can be written in the form

$$k = Z \cdot e^{\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT}$$

Soper[6] has calculated ΔS values for acid and alkaline hydrolysis of ethyl acetate and has compared the experimental values of P with $e^{\Delta S/R}$. It is interesting to note that the calculated value for P agrees fairly well with the entropy factor:

	ΔS	$\log_{10} e^{\Delta S/R}$	$\log_{10} P$
Acid hydrolysis ..	−17·9	$\bar{4}$·089	$\bar{4}$·559
Alkaline hydrolysis ..	−15·1	$\bar{4}$·849	$\bar{4}$·559

Since entropy is a measure of the degree of disorder prevailing in a system and any specific orientation entails a high degree of order, this agreement is but natural and points to the reasonableness of the approach that has been made. The use of the values of total entropy change instead of the entropy of activation does not seriously invalidate the comparison, since the two do not differ appreciably in cases where the activated complex resembles the products of reaction.

From the very close agreement between the calculated value of the P factor and its observed value for a particular solvent (60 or 70% acetone for all the cases cited) it cannot, however, be thought that, in general, this factor alone is the deciding one where large discrepancies in the frequency factor are observed. It has been made abundantly clear in the studies reported in Part III and IV that the composition of the solvent has marked influence on PZ values. At the same time, the present calculations have been useful in bringing out the magnitude and importance of the steric factor in the reaction considered.

I have to thank Dr. S. V. Anantakrishnan for his kind interest in the work.

Summary

Frequency factors for acid and alkaline hydrolysis of esters have been calculated, taking into account the actual shapes of molecules and their necessary orientation at the instant of collision required for the formation of the activated complex. The agreement between calculated and observed values is found to be very satisfactory.

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SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part XIV. Synthesis of Santal

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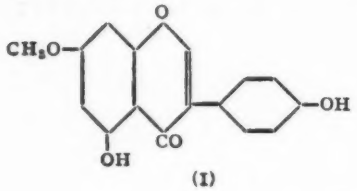
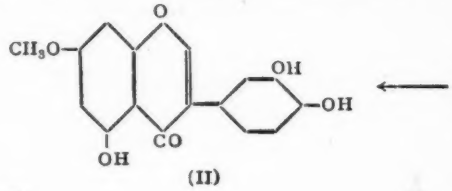
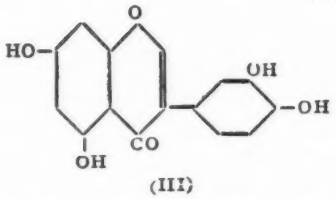
In Part XIII[1] of this series a synthesis of prunetin (I) was described. Santal is a similar isoflavone-7-methyl ether occurring in the wood of Pterocarpus santalinus and its constitution has been recently established as 7-methoxy-5:3′:4′-trihydroxy isoflavone (II) by Robertson and coworkers.[2] The general method of synthesis involving direct methylation should therefore be applicable to this case also. It is now found to be so and santal has been obtained by the partial methylation of nor-santal (III) employing one mole of dimethyl sulphate. However, in the experiment the separation of the resulting mixture is not as simple as in the synthesis of prunetin because of the presence of more hydroxyl groups. The unreacted nor-santal could be removed by dissolution in sodium carbonate; but santal could not be so readily obtained pure by subsequent extraction with sodium hydroxide. It had to be subjected to fractional crystallisation and hence the yield was less.



(I)



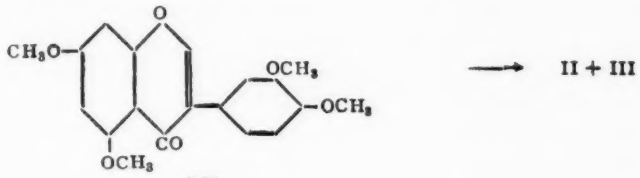
(II)



(III)

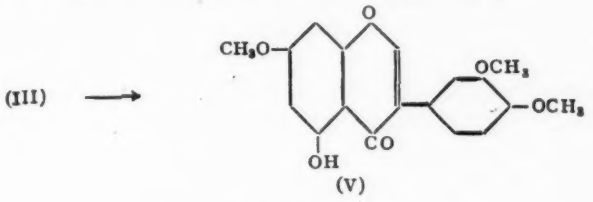
In the course of the preparation of nor-santal (III) synthetically an interesting observation has been made and this may be considered to constitute another synthesis of santal. 5:7:3′:4′-Tetramethoxy isoflavone (IV)

was made by using a variation of the method described by Robertson *et al.*[2] quite similar to the one adopted by us for the preparation of genistein-trimethyl ether and it was subjected to demethylation by boiling with hydriodic acid for one hour. Instead of the expected nor-santal, a mixture was obtained from which santal (II) could be isolated by fractional crystallisation since it is comparatively less soluble. The separation was later made more quantitative by using sodium carbonate for dissolving nor-santal and the mixture was found to consist almost entirely of santal (II) and nor-santal (III). Complete demethylation to nor-santal could be effected by longer boiling with hydriodic acid (3 hours). The santal samples obtained by the two methods were identical and agreed in every respect with the description of natural santal.[2]



(IV)

Besides santal, another partial methyl ether which is readily made from nor-santal is its trimethyl ether (santal dimethyl ether V). Raudnitz and Perlmann[3] reported that by the methylation of santal using dimethyl sulphate and dilute aqueous alkali they obtained a dimethyl ether melting at 141°. We have now carried out the partial methylation of nor-santal using 3 moles of dimethyl sulphate and anhydrous potassium carbonate in dry acetone solution. The product is found to melt at 150–51° and has the properties required for the 5-hydroxy compound (V).



(V)

EXPERIMENTAL

3:4-*Dimethoxy-benzyl cyanide*

This was prepared earlier by Kaufmann and Muller[4] by heating with acetic anhydride dimethoxy-phenyl-acetaldoxime. It has now been made by the more convenient method adopted by Baker and Robinson[5] for the

preparation of 3:4:5-trimethoxy-benzyl cyanide. Starting from veratraldehyde, the first three stages, (1) the azlactone, (2) 3:4-dimethoxy-phenyl pyruvic acid and (3) its oxime have already been described by Kropp and Decker.[6] But in regard to details we have followed the procedure of Baker and Robinson as more convenient. A dry sample of the oxime (10 g.) was heated with acetic anhydride (7 c.c.) on a steam-bath. After the vigorous reaction was over, water (50 c.c.) was added and the mixture cooled in ice; 3:4-dimethoxy-benzyl cyanide separated slowly in the form of colourless flakes. It was filtered, washed with aqueous bicarbonate and water and dried in a desiccator. It crystallised from light petroleum as colourless prisms and melted at 65–6°. Yiled 7 g.

2:4:6-*Trihydroxy-phenyl-3′:4′-dimethoxy-benzyl ketone*

A solution of phloroglucinol (10 g.) and 3:4-dimethoxy-benzyl cyanide (13 g.) in ether (100 c.c.) was treated with zinc chloride (2 g.), was saturated with dry hydrogen chloride for 4 hours and left in the ice chest overnight. The pale yellow ketimine hydrochloride was separated and washed with ether, dissolved in water (100 c.c.) and heated on a boiling water-bath for 2 hours. Even from the hot solution the ketone crystallised out. After cooling it was filtered and recrystallised from dilute methyl alcohol from which it separated in the form of colourless prisms. It melted at 208–10° after losing water at 100°. It gave a purplish red colour with ferric chloride. (Found in a sample dried at 120° for 4 hours: C, 62·8; H, 5·5; $C_{16}H_{16}O_6$ requires C, 63·2; H, 5·3%).

2-*Hydroxy*-4:6-*dimethoxy-phenyl-3′:4′-dimethoxy-benzyl ketone*

The above trihydroxy-dimethoxy ketone (6 g.) was dissolved in dry acetone (200 c.c.), dimethyl sulphate (4 c.c.) and anhydrous potassium carbonate (8 g.) added and the mixture refluxed for 10 hours. Acetone was then distilled off, the residue treated with water and extracted with ether. The ether solution was thrice extracted with aqueous sodium hydroxide (5%) and the combined alkali extract cooled and acidified. The colourless solid that separated out, crystallised from methyl alcohol as colourless needles and rectangular rods melting at 120–21°. It gave a reddish brown colour with ferric chloride and a blue colour with concentrated nitric acid. It agreed in all its properties with the description of Robertson *et al.*[2]

Demethylation

(1) *Santal and Nor-santal.*—5:7:3′:4′-Tetramethoxy isoflavone (1 g.) was dissolved in acetic anhydride (5 c.c.) and treated with cooling with hydriodic acid (12 c.c., d. 1·7). The solution was heated in an oil-bath at 140°

for 1 hour. It was then cooled, decolourised with sulphurous acid and left in the refrigerator overnight. The pale yellow solid that separated was filtered and washed well with water. The crude prouct (A) melted indefinitely between 230° and 240°. It was then crystallised from excess of ethyl acetate. The first fraction that separated on cooling the ethyl acetate solution melted between 210° and 215° and was insoluble in aqueous sodium carbonate. A second crystallisation raised the melting point to 220–22° and further crystallisations did not affect it. The product gave an intense brownish red colour with ferric chloride. From the mother liquor, ethyl acetate was completely removed and the residue macerated with cold sodium carbonate when a part of it was left undissolved. This was filtered, washed with water and crystallised from ethyl acetate when it appeared as colourless rectangular plates and prisms melting at 220–22° and was identical with the above sample. In bulk the solid had a very pale yellow colour. It agreed in all its properties with santal. Total yield 0·2 g. (Found; OCH_3, 10·1; $C_{15}H_9O_5$ (OCH_3), H_2O requires OCH_3, 9·8%; loss on drying 6·0; $C_{16}H_{12}O_6$, H_2O requires loss 5·7%).

The carbonate solution was acidified; the pale brownish yellow solid that separated crystallised from dilute acetic acid in the form of pale yellow globular clusters of minute prisms and needles melting at 269–71°. It gave a green colour changing to a purplish brown with ferric chloride. With concentrated sulphuric acid it developed a yellowish solution becoming blood red on addition of a few drops of concentrated nitric acid. It agreed in its properties with the description of nor-santal (Robertson *et al.*[2]). Yield 0·4 g.

In a repetition of the above demethylation the crude product (A) was directly extracted with aqueous sodium carbonate; the insoluble portion consisting of santal (0·2 g.) crystallised from ethyl acetate as colourless rectangular plates and prisms and melted at 220–2°. The carbonate soluble portion (0·4 g.) consisting of nor-santal crystallised from dilute acetic acid as globular clusters of minute prisms and needles melting at 269–71°.

(2) *Nor-santal.*—The above demethylation using the tetramethoxy isoflavone (1 g.) was done for 3 hours the temperature being maintained between 140° and 150°. The product was worked up as usual. It dissolved completely in cold aqueous sodium carbonate. On crystallising from dilute acetic acid it was obtained in the form of pale yellow globular clusters of tiny prisms and needles and melted at 269–71°. It agreed in its properties and colour reactions with the description of nor-santal. Its acetate, prepared by heating it with acetic anhydride and pyridine, crystallised from ethyl acetate as fine colourless needles melting at 209–10°.

O-Triacetyl santal.—Santal obtained in the above demethylation experiment (0·2 g.) was acetylated by boiling with acetic anhydride (5 c.c.) and a few drops of pyridine for 1 hour. The acetate crystallised from ethyl acetate in the form of clusters of colourless needles melting at 168–70° with sintering at 165°. It agreed in its properties with the description of santal triacetate given by Robertson and coworkers.[2]

O-Triethyl santal.—Santal (0·2 g.) was refluxed in acetone solution with excess of ethyl iodide and potassium carbonate for 20 hours. On filtering and distilling off acetone, the product separated as a viscous oil which solidified to a colourless solid on cooling. It crystallised from alcohol as colourless elongated rectangular prisms melting at 111–12°. It was insoluble in aqueous sodium hydroxide and gave no colour with ferric chloride. It agreed in its properties with the description of *O*-triethyl santal by Robertson *et al.*[2] (Found: C, 68·6; H, 6·6; $C_{22}H_{24}O_6$ requires C, 68·8; H, 6·3%).

Partial methylation of nor-santal

(1) *Santal.*—To a solution of nor-santal (1 g.) in acetone (100 c.c.) dimethyl sulphate (0·3 c.c.) and anhydrous potassium carbonate (1 g.) were added and the mixture refluxed on a water-bath for 4 hours. Acetone was then distilled off and the residue treated with water. The solid that separated was filtered from the carbonate solution, washed once with aqueous sodium carbonate and with water. It was then crystallised from excess of ethyl acetate. The first crop obtained on cooling the solution was found to melt between 180° and 190°. It dissolved partly in sodium hydroxide and gave an intense reddish brown colour with ferric chloride. It was evidently a mixture but it was too small in quantity for further separation. The ethyl acetate mother liquor on further concentration deposited colourless plates. When this was recrystallised from ethyl acetate, it melted at 220–2°. It gave all the colour reactions of santal and a mixed melting point with the sample obtained by the demethylation method was undepressed. Yield 0·1 g.

The carbonate solution on acidification gave nor-santal (0·3 g.) which after crystallisation melted at 269–71°.

(2) *Santal dimethyl ether* (*5-Hydroxy-7 : 3′ : 4′-trimethoxy isoflavone*):—Nor-santal (0·50 g.) was refluxed in acetone solution with dimethyl sulphate (0·55 c.c.) and anhydrous potassium carbonate (1 g.) for 10 hours. On filtering and distilling off acetone from the filtrate, a pale brown solid was left behind. It crystallised from ethyl acetate as colourless needles melting at 150–51°. It gave a deep red colour with ferric chloride and was sparingly

soluble in aqueous sodium hydroxide. (Found; C, 65·4: H, 4·7; $C_{18}H_{16}O_6$ requires C, 65·9; H, 4·9%).

Summary

Santal has been synthesised by methylating 5:7:3′:4′-tetrahydroxy isoflavone with one mole of dimethyl sulphate. When three moles of dimethyl sulphate are employed santal dimethyl ether is obtained. An interesting observation has been made that demethylation of santal trimethyl ether under restricted conditions with hydriodic acid leads to the formation of a mixture of santal and nor-santal. They have been separated using aqueous sodium carbonate.

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ANTHRAQUINONE AND ANTHRONE SERIES

Part VII. A Synthesis of Islandicin

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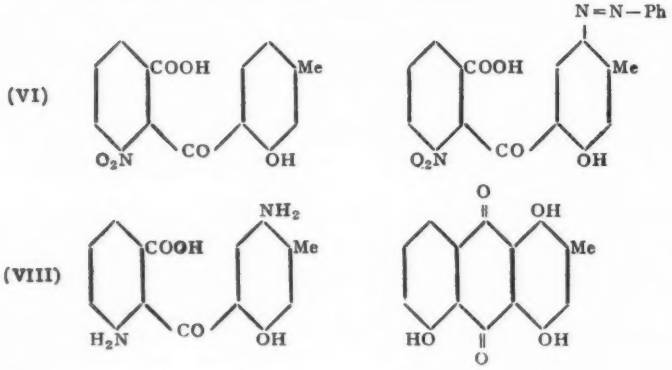
Howard and Raistrick[1] have recently isolated a new coloring matter from the dried mycelium of five different strains of *Penicillium islandicum* Sopp. The compound was a trihydroxy-2-methylanthraquinone, which was converted by oxidation to the known 1:4:5:8-tetrahydroxy-2-methylanthraquinone (cynodontin). It followed, therefore, that the coloring matter must be one of the following four possible trihydroxy-2-methylanthraquinones: 1:4:5- (I), 1:4:8- (II), 4:5:8- (helminthosporin; III) and 1:5:8-trihydroxy-2-methylanthraquinones (IV). Of these, (III) and (IV) are known compounds which were different from the coloring matter of *Penicillium islandicum*. Reduction of the latter gave an anthranol which on oxidation gave the known 4:5-dihydroxy-2-methylanthraquinone (chrysophanic acid; V); of the two compounds (I) and (II), only the former could give (V). Howard and Raistrick therefore assigned to the coloring matter from *P. islandicum* the structure 1:4:5-trihydroxy-2-methyl-anthraquinone (I) and later[2] gave it the trivial name "*islandicin*". The constitution of islandicin has now been confirmed by an unambiguous synthesis.

3-Nitro-2-(2′-hydroxy-4′-methyl)-benzoylbenzoic acid (VI), obtained by the condensation of 3-nitrophthalic anhydride with *m*-cresol,[3] was coupled



(I)

with diazotized aniline in alkaline solution, and the azo dye (VII) was reduced by sodium hydrosulphite in dioxane to 3-amino-2-(5′-amino-2′-hydroxy-4′-methyl)-benzoylbenzoic acid (VIII). The diamine was tetrazotized and the solution poured into concentrated sulphuric acid at 150°, when simultaneous replacement of the amino by hydroxyl groups and cyclization of the benzoylbenzoic acid resulted, yielding 1 : 4 : 5-trihydroxy-2-methylanthraquinone (I), which crystallized from chloroform in dark red lustrous plates, m.p. 218°. The trimethyl ether (IX) crystallized from alcohol in orange-yellow needles, m.p. 161°. The properties of (I) and (IX) were identical with those for islandicin and its trimethyl ether described by Howard and Raistrick.[1]

Experimental

3-Nitro-2-(5′-benzeneazo-2′-hydroxy-4′-methyl)-benzoylbenzoic acid (VII).—Aniline (1·84 c.c.; 0·02 mole), hydrochloric acid (4·8 c.c.) and water (4·8 c.c.) were cooled to 0° and a solution of sodium nitrite (1·0 g.) in water (4 c.c.) was added. The diazonium salt solution was added to a solution of 3-nitro-2-(2′-hydroxy-4′-methyl)-benzoylbenzoic acid (VI)[3] (6·0 g.; 0·02 mole) in 2% sodium hydroxide solution (120 c.c.) during 15 minutes and the mixture stirred below 5° for about one hour. The red solution was acidified with hydrochloric acid. The red-brown dye which separated was filtered (8·0 g.) and crystallized twice from glacial acetic acid when it was obtained as red-brown plates, m.p. 252° (dec.) (Found: N, 10·0. $C_{21}H_{15}N_3O_6$ requires N, 10·3%).

3-Amino-2-(5′-amino-2′-hydroxy-4′-methyl)-benzoylbenzoic acid (VIII).—Sodium hydrosulphite (12·0 g.) was added to a boiling solution of the pure dye (VII; 2·0 g.) in dioxane (30 c.c.) and water (25 c.c.) and the mixture refluxed for 7 hours, during which the color of the mixture changed from red to orange-yellow. The mixture was extracted several times with benzene, the extract concentrated to a small bulk and diluted with ether. The diaminobenzoylbenzoic acid, which separated as a yellow microcrystalline precipitate (2·2 g.), was crystallised from chlorobenzene. The pale yellow plates had m.p. 218° (dec.) (Found: C, 62·4; H, 4·9; N, 9·8. $C_{15}H_{14}N_2O_4$ requires C, 62·9; H, 4·9; N, 9·8%). The diamine (VIII) after diazotization and coupling with an alkaline solution of β-naphthol, gave a red dye, was soluble in ammonia, and gave a hydrochloride with concentrated hydrochloric acid.

1 : 4 : 5-Trihydroxy-2-methylanthraquinone (Islandicin; I).—The above acid (VIII), (0·6 g.) was dissolved in ammonia and reprecipitated with hydrochloric acid (9 c.c.). Aqueous sodium nitrite (0·3 g. in 12 c.c. water) was added to the ice-cold suspension of the acid and the solution kept for 30

minutes below 5°. The solution was gradually poured in concentrated sulphuric acid (35 c.c.) at 150° and the mixture further heated for 15 minutes. After cooling, the purple-red solution was added to crushed ice. The brown-red precipitate (0·4 g.), after two crystallizations from chloroform, gave lustrous dark red plates, m.p. 218° (Found: C, 66·6; H, 4·1. $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7%). The substance is insoluble in 10% sodium bicarbonate, sodium carbonate and ammonia solutions, dissolves in 10% sodium hydroxide solution giving a violet solution, and gives a yellowish orange solution in glacial acetic acid which has a green fluorescence. A solution in concentrated sulphuric acid is bright purple-red in bulk and bluish red in thin layers with a fiery red fluorescence. All these properties have been described by Howard and Raistrick for islandicin.

1 : 4 : 5-*Triacetoxy*-2-*methylanthraquinone*.—A solution of 1 : 4 : 5-trihydroxy-2-methylanthraquinone (0·09 g.) in acetic anhydride (1 c.c.) and 2 drops of pyridine was refluxed for one hour and poured in ice containing a little hydrochloric acid. The brownish yellow precipitate was crystallized twice from alcohol and once from glacial acetic acid; the pale yellow needles had m.p. 208° (Found: C, 63·6; H, 4·3. $C_{21}H_{16}O_8$ requires C, 63·6; H, 4·1%).

The melting points of synthetic 1 : 4 : 5-trihydroxy-2-methylanthraquinone and its triacetyl derivative were undepressed when mixed with natural islandicin and its triacetyl derivative.

1 : 4 : 5-*Trimethoxy*-2-*methylanthraquinone* (*IX*).—1 : 4 : 5-Trihydroxy-2-methylanthraquinone (84 mg.), boiling dry acetone (10 c.c.), dimethyl sulphate (0·4 c.c.) and anhydrous potassium carbonate (0·4 g.) were refluxed for 10 hours. The yellow solution was filtered and the residue extracted with hot acetone. The residue obtained after removal of the solvent under reduced pressure, crystallized from alcohol in orange-yellow needles, m.p. 161° (Howard and Raistrick, 161°) (Found: C, 69·2; H, 5·2. $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·2%). The trimethoxy derivative is insoluble in 10% sodium hydroxide, dissolves in concentrated sulphuric acid, giving a blue solution with a faint purple fluorescence.

Summary

The constitution (I), assigned by Howard and Raistrick[1] to islandicin, the coloring matter from the dried mycelium of *Penicillium islandicum* Sopp., has now been confirmed by unambiguous synthesis.

3-Nitro-2-(5′-benzeneazo-2′-hydroxy-4′-methyl)-benzoylbenzoic acid (VII), obtained by coupling 3-nitro-2-(2′-hydroxy-4′-methyl)-benzoylbenzoic acid

(VI) with diazotized aniline, gave on reduction 3-amino-2-(5′-amino-2′-hydroxy-4′-methyl)-benzoylbenzoic acid (VIII). The latter was converted in one step to 1 : 4 : 5-trihydroxy-2-methylanthraquinone (I) by tetrazotization and treatment with hot sulphuric acid. The properties of (I), its triacetate and its trimethyl ether are identical with those of islandicin, its triacetate and its trimethyl ether described by Howard and Raistrick.

We are greatly indebted to Prof. H. Raistrick, F.R.S., for sending us specimens of natural islandicin and its triacetyl derivative.

We are also indebted to the Council of Scientific and Industrial Research under whose auspices this work was carried out, and to Mr. T. S. Gore for the microanalyses recorded in the paper.

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INTENSITY RATIO OF THE RAMAN LINES IN DIAMOND

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1. Introduction

As is well known, with moderate exposures the Raman spectrum of diamond consists of only one intense line with a frequency shift of 1332 cm.$^{-1}$ With the use of the λ 2537 radiation of the mercury arc for excitation and long exposures, the most striking feature noticeable in the spectrum is the appearance of a whole series of sharply defined lines belonging to the second order spectrum and also the anti-Stokes line corresponding to the principal frequency shift 1332 cm.$^{-1}$ An accurate determination of the intensity ratio of the first and second order Raman lines in diamond is of great theoretical interest. Besides, a measurement of the intensity ratio of the Stokes and anti-Stokes lines of the principal frequency affords a reliable verification of the dependence of intensity of Raman line on the fourth power of the emission frequency (Placzek, 1934). Diamond is the most suitable case for this purpose as it is the one substance in which the anti-Stokes line corresponding to the highest frequency shift has so far been recorded.

According to Placzek's theory of the scattering of light, the ratio of the intensities of the Stokes to the anti-Stokes Raman line is given by

$$\frac{I_S}{I_{AS}} = \left(\frac{\nu - \nu_i}{\nu + \nu_i}\right) e^{\frac{h\nu_i}{kT}}, \qquad (1)$$

where $\nu - \nu_i$ and $\nu + \nu_i$ are the respective emission frequencies. Experimental verification of this relation has so far been carried out for Raman lines with frequency shifts less than 500 cm.$^{-1}$ For lines with $\nu_i < 600$ cm.$^{-1}$, the first term on the right-hand side of equation (1) will be very nearly equal to unity and the preponderance of the exponential term makes an experimental verification of the dependence of the ratio on the emission frequency very difficult. Though for high-frequency-shift Raman lines and visible radiations of the mercury arc for excitation, the frequency factor deviates considerably from unity, it is not experimentally possible to record the anti-Stokes components of these Raman lines with sufficient intensity on a clear

background under excitation in the visible region. Another serious limitation is that for an accurate determination of heterochromatic intensity ratios, the photographic density ratio should not exceed 6–8. The first difficulty is easily overcome by the use of λ 2537 for exciting the Raman spectrum. In order to measure accurately the ratio of the intensities of the Raman lines, it is necessary to employ the new method of using a Spekker photometer outlined by one of us in an earlier communication (P. S. Narayanan, 1948), especially when the Stokes–anti-Stokes ratio exceeds 10. Using this method the relative intensities of the Stokes and anti-Stokes components of the 1332 line and also of the prominent second order lines of diamond have been measured. The results are given below.

2. Experimental Details and Results

A semi-circular piece of diamond (Catalogue No. N.C. 174 in Sir C. V. Raman's personal collection) 1·5 mm. thick was employed. It was transparent to the ultra-violet region with a sharp cut off at λ 2350. By the use of the continuous radiations of a hydrogen lamp it was confirmed that the specimen had no appreciable absorption till the very absorption limit. The plate of diamond was held in the spark gap of a Hilger ultra-violet Spekker photometer with its broad face vertical and its straight edge facing the quartz rhombs. The λ 2537 radiation of a quartz arc was focussed on the diamond with a short focus lens of aperture 2″. By suitable adjustment of the focussing lens and the plate of diamond, the scattered light was made to be of uniform intensity over both the apertures of the Spekker photometer. The light emerging from the photometer was allowed to fall on the slit of a medium quartz spectrograph. The graduated drum of the photometer was set exactly at 2 so that the variable aperture had an area 1/100 that of the fixed aperture. In the spectra obtained thereby, one could effect a direct comparison of the Stokes and anti-Stokes Raman lines and also the second-order lines. The Stokes component of the 1332 Raman line in the spectrum obtained through the fixed aperture appeared in 5 minutes, while the second order lines and the anti-Stokes of 1332 were recorded with an exposure of two days.

The relative intensities were computed using the density-log intensity curve for a mean λ 2540. As mentioned in the previous paper, in the case of the photographic plates used by the authors, the variation of photographic sensitivity in the region λ 2450–2650 was very small. Even if there is any slight decrease of sensitivity with decrease of λ, it would tend to increase the Stokes-anti-Stokes ratio—a point which will be discussed later in the paper. The results are summarised in Tables I and II. In the case of the

TABLE I. *Stokes–anti-Stokes ratio for the* 1332 *Raman line*

$\Delta\nu = \nu_i$	$e^{\frac{h\nu_i}{kT}}$	$\left(\frac{\nu-\nu_i}{\nu+\nu_i}\right)^4$	$\left(\frac{\nu-\nu_i}{\nu+\nu_i}\right)^4 e^{\frac{h\nu_i}{kT}}$ Theoretical	Observed value
1332	581	0·763	443	426

TABLE II. *Relative intensities of the principal second-order Raman lines*

cm^{-1}.	$I_{1332}/I_{S.O.}$
2160	590
2460	130
2665	270

second-order spectrum, there is a group of closely spaced lines at about 2460 cm.$^{-1}$ Their peak intensity has been estimated.

3. DISCUSSION

The possible sources of error in the measurements described above are the following:

(1) The difference in the sensitivities of the photographic plate for the regions λ 2450 and λ 2625 where the anti-Stokes and Stokes lines respectively fall.

(2) The influence of the ultra-violet absorption frequency of diamond on the intensity.

(3) General background arising from the long exposures used.

Although no accurate measurements of the relative photographic sensitivities for λ 2450 and λ 2625 were carried out, the indications were that the difference if any was very small. Even if there was a small difference, its effect would be to increase the Stokes–anti-Stokes ratio and thus bring the observed value closer to that given by the Boltzmann factor alone.

If one takes into consideration the influence of the absorption frequency of the scatterer, the intensity ratio is given by the following equation:—

$$\frac{I_S}{I_{AS}} = \left(\frac{\nu-\nu_i}{\nu+\nu_i}\right)^4 e^{\frac{h\nu_i}{kT}} \Big/ \left(1 + \frac{4\nu\nu_i}{\nu_a^2 - \nu^2}\right), \qquad (2)$$

where ν_a is the absorption frequency. The principal electronic frequency of diamond which is effective in dispersion corresponds to λ 1750. Besides, as there is no absorption even at λ 2360, it can be shown that the denominator in equation (2) is nearly equal to unity, *i.e.*, the intensity ratio is given by equation (1).

As for the third source of error, it may be pointed out that the chief advantage in using ultra-violet excitation is the fact that the Raman lines appear in the region of the spectrum which is free from any continuum. In the case of diamond, the Stokes component happens to coincide almost with the mercury line λ 2652·2. But by a proper adjustment of the arc and the aperture through which the scattered light was taken, it was found possible to cut down the parasitic illumination to an extent where the Raman line was brighter than even the strongest line of the mercury triplet with a mean wavelength 2653. Under such conditions it is needless to say that the contribution of the mercury line to the intensity of the Raman line in the spectrum obtained through the reduced aperture was practically zero.

The observed value of the Stokes–anti-Stokes ratio agrees well with that calculated using equation (1) confirming thereby in a decisive way the dependence of the intensity of the Raman line on the fourth power of the emission frequency.

A reasonably quantitative idea of the relative intensities of the first and second order lines in the case of C–C oscillation can be obtained by a calculation similar to that carried out by Bhagavantam (1939) in the case of some diatomic molecules. Using the values given by Jevons for ν_0 ($= 1641 \cdot 5$ cm.$^{-1}$) and $\nu_0 x$ ($= 11 \cdot 67$ cm.$^{-1}$) for C_2 from band spectra data, the ratio of intensity of the fundamental to that of the octave has been calculated and is given by

$$\frac{\nu_f^4 a_{01}^2}{\nu_h^4 a_{02}^2} = 318,$$

the frequency factor being calculated by taking λ 2537 as the exciting line. It is seen that the value obtained in the case of diamond for the 1332 line and its octave (Table II) is remarkably close to this. A rigorous calculation of the ratio, however, requires a knowledge of the potential energy and wave function in the case of diamond.

In conclusion, the authors wish to express their gratitude to Prof. C. V. Raman for a loan of the diamond and to Prof. N. Seetharaman of the Presidency College, Madras, for lending the Spekker photometer without which the above investigation would not have been possible.

Summary

The relative intensities of the Raman lines in diamond have been studied by the spectrophotometric method, outlined in an earlier communication, using an ultra-violet Spekker photometer in conjunction with a medium quartz spectrograph.

The values obtained for the fundamental oscillation, 1332 cm.$^{-1}$ are:—

$$I_{Stokes}/I_{anti\text{-}Stokes} = 426$$

$$I_{Fundamental}/I_{Octave} = 270$$

confirming thereby the dependence of the intensity of a Raman line on the fourth power of the emission frequency.

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ERRATUM

Vol. XXXII, No. 3, Page 190, last word in 8th line from the top:—
For " the " *read* " to ".